## **Reclamation of copper-base scrap and residues**

### A. K. BHATTACHARYYA

THE importance of secondary metals and alloys in copper and copper alloy industries is recognised when one considers that even in U. S. A., a country fairly rich in copper ores, about half the consumption of copper is accounted for by secondary metals. When such is the case, there is every reason to believe that India can benefit substantially by improving its secondary copper and copper alloy industries as not only is our country relatively poor in copper ore deposits, but also her demand for copper, anticipated as 238 thousand tonnes in 1970-71 would be more than 15 times its estimated licensed capacity— 16.5 thousand tonnes of fire refined blister copper at the end of the Fourth Plan.<sup>1</sup>

The Railways are one of the largest consumers of non-ferrous metals in this country, their holdings of non-ferrous metals are estimated to exceed Rs 21 crores<sup>2</sup> and a substantial portion of this amount is accounted for by the copper and copper-base alloys, the principal non-ferrous metal used on the Railways. The annual outturn of the railway non-ferrous foundries amounts to about 23 thousand tonnes and the accumulations of non-ferrous scrap at the end of March 1967 were reported as 11 400 tonnes<sup>3</sup> and the value was estimated at Rs 2.62 crores. The railways reclaim most of their known non-ferrous scrap arisings in their foundries ; during the year 1966-67, 19 604 tonnes of non-ferrous scrap, mostly copper-base, was utilised by the railways for their own use and 1469 tonnes was disposed of to the trade.

The work associated with the conversion and utilisation of copper-base scrap on the railways have been published earlier<sup>2</sup>, further details regarding classification, segregation and reclamation not included in earlier publications, are presented in this paper. Important aspects of sorting, pre-treatment and reclamation of copper-base scrap and residues containing high proportion of zinc, have also been discussed from published information on the subject, and the work undertaken in this connection in the Research, Designs and Standards Organisation has been described.

#### Classification, segregation and sorting of copper-base scrap

The need for a rationalised system of classification

#### SYNOPSIS

Important aspects of classification, sorting and pretreatment of different categories of copper-base scrap have been discussed. Reclamation procedure adopted on the Railways in this connection has been described. Refining methods available for conversion of mixed copper-base scrap containing high proportion of zinc and the work recently undertaken in the Research Designs and Standards Organisation in this regard and methods of treatment of mixed oxides formed during refining of mixed copper-base scrap have also been mentioned.

in eliminating ambiguity arising from varying interpretations of commonly used terms in the field of non-ferrous scrap have led to the adoption of such system of classification and coding of non-ferrous scrap metals and alloys in different countries based on prevailing trade practices and recognised usage.

The Railways have adopted a system of classification of non-ferrous scrap since 1958 in which the copper and copper-base scrap have been broadly categorised under copper, bronze and brass. These have been further classified according to their form viz. lumps, turnings; according to their chemistry viz. arsenical copper, electrolytic copper, phosphor bronze, gun metals, loaded bronze, brass. Finely divided scrap e. g. turnings have been further sub-classified into mixed and unmixed qualities. Copper-base residues have also been classified. I. S. I. has brought out a coding and classification for non-ferrous scrap metals and residues in 1962. Similar systems of classification are also in existence in U. K. and U. S. A. The portions applicable to copper and copper-base alloys in the above systems are set out in a tabular form in Appendix I.

The fact that some amount of intermixing occurs in the case of machine shop non-ferrous scrap arisings has been accepted in all the systems though it is generally realised that admixture of various grades of scrap affects the economics and ease of their conversion. Railways are no exception and here again the machine shops are the places where most of the contamination occurs. In machine shops, attached to large repair shops, steady runs of the same grade of non-ferrous alloys are seldom expected. Moreover, the operators interested normally in the machining part

Mr A. K. Bhattacharyya, Deputy Director (Metallurgical), Research Designs and Standards Organisation, Ministry of Railways, Chittaranjan.

of his job may not bother much about the scrap. Under the situation, it is but natural that most of the contamination should occur in the machine shops.

Once having spent time and money for initial segregation in machine shops and foundries, preventing admixture of the segregated scrap during subsequent handling and storage becomes more and more important. Existing procedures on the railways require that the non-ferrous scrap arisings are returned to the stores depots after segregation into distinct categories as per railway classification. There is, however, often a need for further sorting and segregation of the scrap receipts in the stores yards.

Discussion on scrap segregation is not complete without a reference to sorting procedures. Though questions are raised at times about the costs involved in elaborate sorting procedures, it has to be considered that the quality of the secondary alloys and the economics of their production largely depend on the effectiveness of sorting of the charge and sorting at this stage should be more profitable than sorting in furnace. Inadequate sorting leading to gradual build up of tramp elements in secondary alloys would also bring in an undesirable trend of progressive down-grading of the products. Farthing<sup>4</sup> mentions that in non-ferrous scrap sorting, there is just no substitute for experience. Muchrie<sup>5</sup> elaborating further states that normal testing procedures by visual examination with regard to shape, pliability, hardness, magnetic properties, colour and types of fresh fractures may not be sufficient guarantee against adequate sorting. It is, however, considered that in case of worn components and lump scraps of phosphor-bronze, lead-bronze, gun metals, brass plated scrap, claddings, etc. simple sorting by shapes, colour, filling, sawing, etc. with implements such as magnifying glass, file, hack saw, magnet, small portable drill can be applied with considerable success. Colour sorting is also possible to distinguish phosphor-bronze from leaded bronze, swarf when the lead content is about 10% or more. It is, however, difficult to colour-sort leaded bronze, leaded gun metal and leaded brass maganese bronze from each other. Drill sorting may be resorted to after colour-sorting in case of scrap having marked difference in machinability or to facilitate colour sorting in case of tarnished, plated or coated scrap. In doubtful cases, simple spot tests may help. Tandon and Banerjee<sup>6</sup> detailed some rapid spot testing methods with nitric acid, silver nitrate, ammonia, etc. In case of mixed up finely divided scrap drawn from different sources, there is no shortcut and complete melting of sample charges has to be undertaken to ascertain the average analysis. It is important in such cases to adopt sampling procedures so that the melt is representative of the lot as far as practicable.

#### Pre-treatment of copper-base scrap

Pre-treatment is necessary for improving quality and to facilitate handling, storage and charging of the scrap. Iron and steel attachments are removed, white metal lining melted down and separated and large pieces broken down into small ones to suit the melting units.

Insulations are either stripped or burnt and the wires compressed or bundled to facilitate charging. Grease and oil present are removed by alkali bath treatment and moisture by pre-drying. Oil or grease may lead to defective castings offsetting completely the economic advantage gained from the use of scrap and extra moisture in the charge results in proportionate loss in melting time, labour and furnace capacity. Detergents may be useful in reducing surface tension of water-oil emulsion when excess moisture and oil in swarf are centrifuged out. Pre-drying is carried out in kiln driers where large quantities are involved, for fine residues (above 60 mesh), however, kiln drying may entail uneconomic loss of fine metallics through the flues. Where bronze swarf is not mixed with white metal, briquetting after separation of ferrous contaminants is advantageous as not only is the charge compressed into denser shapes, but also substantial quantity of water and oil gets removed in the process.

Light metal swarf, stored under unfavourable condition, may carry as much as 10-20% oxides<sup>7</sup> and it is also known that metal losses in dross becomes disproportionately high with increasing oxide content of the charge. In case of swarf, containing 5% or more of oxides, therefore, flux in adequate proportion may be incorporated in the briquettes to enable quicker and better fluxing action during melting.

#### Per-treatment of residues

Skimmings, slag, dross, etc. are first broken down. During the process, the non-metallics break off very easily and by simple screening it can be separated into two groups (i) fines containing about 10% metallics, (ii) coarse particles containing about 90% of the metallics.<sup>8</sup> Usually seiving through 60 and 100 mesh should be satisfactory. More metallics may be recovered by going higher, but most of the fines above 100 mesh will find its way back in the skimming, dross or slag a vicious cycle without profitable results.

The importance of small details such as screening of moulding sands in non-ferrous foundry for re-use is often not appreciated but such procedures not only clean the moulding sand but also work out as a profitable source of non-ferrous scrap, amply compensating the cost of labour and implements involved in such use. Similarly, discarded crucibles, worn out refractories from ladles may lead to fruitful sources of scrap. Such materials in non-ferrous foundries should, therefore, be examined and procedures formulated for reclamation where profitable.

### Reclamation of copper and copper-base alloy scrap arisings

For lumps, turnings and swarf, sorted into distinct grades, commercially free from ferrous or white metal contaminants, straightforward melting is adopted in crucible rotary or reverberatory furnaces under cover of suitable flux. The procedures are well-know and some important aspects are only discussed here.

Reverberatory melting, advantageous for lump scrap.

is not favoured for fines as oxidation and flue losses are high. The swarf or turnings are charged in as concentrated form as possible for maximum utilisation of the available melting capacity. The crucibles or hearth are pre-heated to 700°C-800°C before charging and partly filled with molten metal of similar composition. This helps quicker heating and prevents undue oxidation of finely divided charge. Besides, the molten metal also protects the lining of the hearth from reacting with the flux. Fluxes are well distributed with the charge particularly in case of swarf or turnings to maximise fluxing action during melting. The melting point of the flux should not be so low as to allow it to run away before exerting its refining action.

#### Reclamation of mixed copper-base scrap and residues on the railways

For reclamation of bronze borings mixed with white metal, Sigma oil process, Bradly process and differential melting processes are known.

The differential process, in which the separation is achieved by differential melting of the high and low melting constituents in the mixed scrap, is under operation on the N. E. Railways with considerable success. Briefly, the process operates on the following steps: (i) Bronze swarf mixtures, mixed with ferrous and white metal ingredients but free from contamination, are first passed through magnetic separators which remove the ferrous ingredients. The capacity of the separator used on the N. E. Railway is about 0.25 tonnes per hour for swarf containing about 3% ferrous ingredients. (ii) The bronze swarf mixed with white metal is then fed into a cylindrical 12 mesh sieve in which the charge is moved forward by a screw arrangement fitted to the shaft. During forward movement of the charge, the sieve retains almost all the white metal and the coarser particles of bronze swarf. The finer bronze swarf pass-ing through is collected separately. (iii) The coarse mixture of bronze and white metal swarf is then fed into a second cylindrical 16 mesh sieve rotating at a speed of 14 rpm. The sieve is kept at a temperature of about 350°C. The forward movement of the charge is also achieved by a similar screw arrangement as in the first drum. During the forward movement of the charge, the white metal portion of the swarf melts and trickles through the sieve and gets collected in trays. The bronze swarf, practically free from white metal, is discharged through the end of the second rotating sieve. (iv) The bronze borings collected from the first and second sieve are melted in a rotary furnace of one ton capacity and ingotted. The details of the plant are shown in Fig. 1.

The capacity of the plant is about 80 kg per hour, which requires one semi-skilled and one unskilled labour for operation. On an average, it has been observed that the mixed bronze swarf contains about 4 to 5% antimony. The fine bronze swarf passing through 12 mesh sieve in the first operation shows an average antimony content of about 0.54%. The analyses of the bronze borings after the separation of white metal averages—tin 7-8\%, lead 9-10\%, antimony .05-.07%,

#### Bhattacharyya : Reclamation of copper-base scrap and residues

others generally below 0.5%, and copper remainder.

#### Reclamation of residues

Reclamation of residues of copper-base alloys usually involves milling, sieving, concentrating and fire-refining. The copper-base residues recovered from screening of moulding sands, discarded crucibles, worn out refractories of ladles, etc. in non-ferrous foundry can also be reclaimed along with other residues in a similar manner.

The salient features of the process of reclamation adopted for bronze residues such as slag, clinkers, dross, ash metal, etc. on the E. Railways are summarised here: (i) milling of the residues in Surki mills, (i) milled residues are fed on to vibrating wilflay tables in which the fines i.e. non-metallics, mostly sand, are washed away with water and the coarse particles containing metallics are carried forward to one end of the table and collected, (iii) the collected concentrate containing metallics is air-dried by spreading on floor and after which it is fed to magnetic separators, (iv) after separation of ferrous ingredients the concentrate is sieved. The fines passing through contain about 2% metallics and the coarse particles retained are charged into a reverberatory furnace of 1 ton capacity and melted with a flux composed of soda ash, common salt and borax in the ratio of 4:2:1 by weight. The flux is used at the rate of 1%of the weight of the charge.

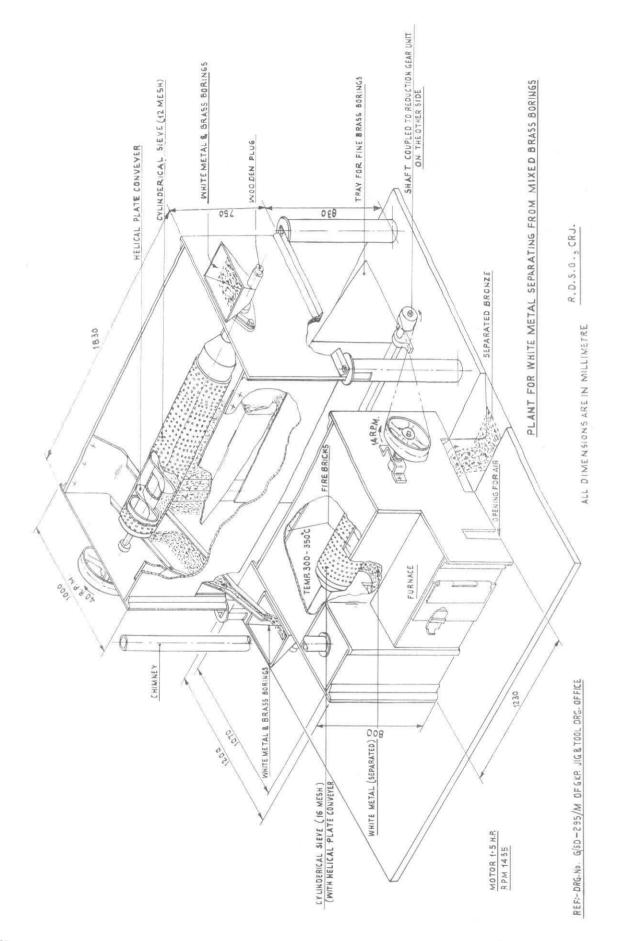
All handling is done manually and four unskilled labourers are employed in each shift to feed the Surki mills and welflay tables. The average monthly outturn is about 22 tonnes of washed concentrate from which about 10–15 tonnes of ingots depending on the metallic contents of the concentrates are reclaimed per month. The analyses of the reclaimed ingots indicate that these could be converted easily into class III-IV bronzes conforming to IS : 1458. The chemical composition of the reclaimed ingot averages Sn 5–7%, Pb 8.5–9.5%, Fe 0.3% max., Zn-trace and Cu-balance.

#### Reclamation of mixed bronze scrap contaminated with brass and brass scrap

A substantial amount of non-ferrous scrap arising on the railways falls under this category. The Railways at present offer these arisings to the trade.

ways at present offer these arisings to the trade. In published literature, ditails of various refining methods for copper-base scrap containing lead, tin and zinc as alloying elements have been described. Some of these can be successfully applied for reclamation of mixed bronze scrap containing brass or mixed brass scrap.

W. S. Nelmes<sup>9</sup> et al. have reported on the experimental work on top jetting oxygen process in replacing the conventional conversion process of black copper in plain converters. The experimental work and trials indicated satisfactory results. Copper tubing, protected with refractory coating was used for oxygen jetting. The sequence of operation adopted was





(i) charge 1-ton black copper at about 1100°C, (ii) blow oxygen for 8 minutes at the rate of 60 cft. per minute when most of the Fe and Zn is eliminated, (iii) continue blow at the rate of about 50 cft. per minute or less adding 100 lb of silica over a period of 5 minutes, (iv) continue blow till 1800 cft of  $O_2$ had been introduced, (v) stop blow and add 30 lb of coke to protect copper from oxidation.

It has been claimed that black copper containing 70-75% Cu, 5-10% Sn, 3-5% Zn, 2-4% Fe and 2-4% Ni obtained from smelting of copper slags, dross, residues, etc. in the blast furnace, could be converted within about 35 minutes to refined copper containing about 96-97% copper traces of tin, iron, zinc and antimony with about 0.6% lead and 1% nickel. The operating cost had been claimed to be similar to that of the converter process though capital investment is low.

Other methods in this field have been described by Whitekar.<sup>10</sup> Tandon and Banerjee<sup>6</sup> also reported details of such processes. Amongst these the following may be mentioned, particularly for treatment of brass-bronze scrap mixtures.

The process patented by Lissauer et al. in which selective oxidation of the alloys was brought about by blowing reducing gases through the melt while maintaining a reducing atmosphere above the melt in the first stage when zinc was volatilised which was burnt to oxide and collected at the mouth of the furnace. After removal of zinc, tin was eliminated and tin-rich oxide fumes were collected when oxidising atmosphere was brought about above the melt. It was claimed that a charge containing about 80% copper, 3-7% tin, 2-3% lead and balance zinc could be converted to refined copper containing 98.25% copper, tin and lead less than '15% each. The compositions of the first and second oxide fumes were reported as zinc 70-71%, lead 7-8%, tin 0.2-0.3% and zinc 5-14%, lead 14-28%, tin 56.12%, copper 0.32% respectively. The slag formed in the process is about 2.5% of the melt.

A process was described by Kohlmeyer in which brass scrap was melted in an oil-fired rotary furnace and then heated to drive off zinc preferentially from the melt which burnt to oxide and was collected through an electrostatic precipitator. It was claimed that no copper slag was produced; a scrap containing 72% copper, 22.8% zinc, 2.8% tin, 2.7% lead and 0.22% iron analysed 92.98% copper, 0.74% zinc, 3.7% tin, 2.36%lead and 0.03% iron at the end of 5 hours. The oxide fume produced at the end of 1 hour analysed 80% zinc, 1.45% and 0.15% of lead and tin respectively and that after 5 hours was 74.2% zinc, 7.15% and 0.68% of lead and tin respectively.

The unique feature of the Poland process described for treatment of brass scrap was that zinc of about 98% purity could be distilled out directly from brass melt in Wilkin's Poland Distillation furnace. It was claimed that 85-92% of the zinc and about 95% of the copper present in the scrap could be recovered in the process and the zinc content in the residual melt was about 2\%, which could be used directly for manufacture of brass ingots or further refined in a converter to tough pitch copper. Reclamation work undertaken in R. D. S. O. for conversion of copper-base scrap containing high proportion of zinc

Work on conversion of copper-base scrap containing high proportion of zinc has been recently undertaken in R. D. S. O. The experimental trials undertaken and the results so far obtained were as follows:

Mixed scrap arisings, stated to contain high proportion of zinc, were procured from the railways. The first lot of scrap procured analysed Sn 0.23%, Pb 1.80%, Zn 26.17%, Cu 66.20% and the second lot analysed as Sn 3.3%, Pb 1.48%, Zn-9.7%, Cu 82.78%.

The scrap charge was melted in oil fired crucible furnace of 50 kg capacity. The molten metal was tapped in a pre-heated fire clay lined handout ladle of 50 kg capacity in which oxygen lancing was carried out. The lancer used was made up of 12 mm dia. copper tube having 3 mm wall thickness. About 450 mm length from the tip of the lancer was protected with asbestos rope and coated with magnesite powder and clay. The lancing was carried out intermittently and samples were taken at intervals.

TABLE I Experimental details and results obtained

1.Weight of the charge21:08 kg40:78 kg2.Nature of the chargeFirst lot, analysis given aboveSecond lot analysis given above3.Melting time1 hr 30 mts1 hr 45 mts4.Oxygen rate used for lancing36 cft/hour18 cft/hour5.Weight of metal obtained after lancing3:27 kg36:61 kg6.Weight of slag obtained13:27 kg2:17 kg7.Yield %62:989:88.RemarksVolatilisation losses of zinc and process metal losses were highVolatilisation losses or zinc and process metal losses were comparatively low				NON-RELEVANCE AND
chargegiven abovegiven above3. Melting time1 hr 30 mts1 hr 45 mts4. Oxygen rate used for lancing36 cft/hour18 cft/hour5. Weight of metal obtained after lancing3.27 kg36.61 kg6. Weight of slag obtained13.27 kg2.17 kg7. Yield %62.989.88. RemarksVolatilisation losses of zinc and process metalVolatilisation losses of zinc and process metal losses were	1.		21.08 kg	40.78 kg
<ul> <li>4. Oxygen rate used for lancing</li> <li>5. Weight of metal obtained after lancing</li> <li>6. Weight of slag obtained</li> <li>7. Yield %</li> <li>8. Remarks</li> <li>8. Remarks</li> <li>Yolatilisation losses of zinc and process metal losses were metal losses were</li> </ul>	2.			Second lot analysis given above
<ul> <li>used for lancing</li> <li>5. Weight of metal obtained after lancing</li> <li>6. Weight of slag obtained 13.27 kg</li> <li>6. Weight of slag 13.27 kg</li> <li>7. Yield %</li> <li>8. Remarks</li> <li>8. Remarks</li> <li>Yolatilisation losses of zinc and process metal losses were metal losses were</li> </ul>	3.	Melting time	1 hr 30 mts	1 hr 45 mts
metal obtained after lancing0006. Weight of slag obtained13.27 kg2.17 kg7. Yield %62.989.88. RemarksVolatilisation losses of zinc and process metalVolatilisation losses of zinc and process metal losses were	4.	used for	36 cft/hour	18 cft/hour
obtained       7. Yield %       8. Remarks       Volatilisation       Volatilisation       of zinc and process       process metal	5.	metal obtained	3.27 kg	36 <sup>.</sup> 61 kg
8. Remarks Volatilisation Volatilisation losses losses of zinc and of zinc and process process metal metal losses were	6.	Weight of slag obtained	13 <sup>.</sup> 27 kg	2.17 kg
losses of zinc and of zinc and process process metal metal losses were	7.	Yield %	62.9	89.8
	8.	Remarks	losses of zinc and process metal	of zinc and process metal losses were

#### Results of progressive analysis and temperature of the melt recorded during oxygen lancing

In order to assess the possibility of application of the oxygen lancing process in ladles for reclamation of mixed bronze-brass scrap, further experimental trials are considered necessary. The limited experiments carried out, however, indicate that by regulating the oxygen Bhattacharyya : Reclamation of copper-base scrap and residues

#### TABLE II First experimental heat

					Temp°C	Cu %	Sn %	Pb %	Žn %	$R_2O_3\%$
sample	before	1:	incing		1100°C	66.22	0.23	_	26.05	2.5
2.5	after	1	min.	,,	**		0.53	1.90	23.80	2.0
3.2	32	3	5.2	,,	33	_	_	2.11	20.59	1.9
3.5	,,	5	,,	÷,	,,	_	0.23	2.11	13.34	1.0
2.2	2.9	$6\frac{1}{2}$	33	,1	5.1	_	0.22	-	9.18	0.6
3.5	22	$7\frac{1}{2}$	,,	,,	1070°C	88.22	0.31	2.93	7.98	0.2
	25 72 23	,, after ,, ,, ,, ,,	,, after $\frac{1}{2}$ ,, ,, 3 ,, ,, 5 ,, ,, $6\frac{1}{2}$	,, after $\frac{1}{2}$ min. ,, ,, 3 ,, ,, ,, 5 ,, ,, ,, $6\frac{1}{2}$ ,,	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	sample     before     lancing     1100°C       ,,     after     1/2     min.     ,,     ,,       ,,     3     ,,     ,,     ,,       ,,     5     ,,     ,,     ,,       ,,     5     ,,     ,,     ,,	sample       before       lancing       1100°C       66·22         ,,       after $\frac{1}{2}$ min.       ,,       ,,       -         ,,       after $\frac{1}{2}$ min.       ,,       ,,       -         ,,       ,3       ,,       ,,       ,,       -         ,,       ,5       ,,       ,,       ,,       -         ,,       ,5       ,,       ,,       ,,       -         ,,       ,5       ,,       ,,       ,,       -         ,,       ,5       ,,       ,,       ,,       -	samplebeforelancing1100°C66.220.23,,after $\frac{1}{2}$ min.,,	samplebeforelancing1100°C $66\cdot22$ $0\cdot23$ $-$ ,,after $\frac{1}{2}$ min.,,,,,, $ 0\cdot23$ $1\cdot90$ ,,,,3,,,,,, $  2\cdot11$ ,,,,,5,,,,,, $ 0\cdot23$ $2\cdot11$ ,,,5,,,,,, $ 0\cdot23$ $2\cdot11$ ,,, $6\frac{1}{2}$ ,,,,,, $ 0\cdot25$ $-$	samplebeforelancing1100°C $66.22$ $0.23$ $ 26.05$ ,,after $\frac{1}{2}$ min.,,,, $ 0.23$ $1.90$ $23.80$ ,,,, $3$ ,,,,,, $  2.11$ $20.59$ ,,,,,5,,,,,, $ 0.23$ $2.11$ $13.34$ ,,, $6\frac{1}{2}$ ,,,,,, $ 0.25$ $ 9.18$

#### TABLE III Second experimental heat

						Temp.°C	Cu %	Sn %	Pb %	Zn %	$R_2O_3\%$
lst san	nple	before	lanci	ing		1120°C	82.8	3.0		9.7	1.0
2nd	,,	after	11	min.	,,	-		3.2	1.60	9.31	1.0
3rd	1.1	21	3	.,	,,	1180°C	-	3.3	1.63	8.84	1.0
4th	,,	۰,	5	.,	,,	1100°C		-	_	7.46	
5th	3.1	• •	7	••	,,	1060°C	87.0	4.5	1.65	6.64	0.2

lancing rate it may be possible to minimise volatilisation losses of zinc by retaining most of it in the slag (Tables II and III). Slower rate of oxygen lancing is also expected to reduce process metal losses. It is also considered that in presence of sufficient proportion of zinc in the melt, the losses of tin and lead during oxygen lancing will be negligible. Further experiments have been programmed accordingly.

#### Treatment of mixed oxides formed during conversion of mixed copper-base scrap and their recovery

Except for the Poland distillation process, the processes discussed in this paper for reclamation of mixed copper base scrap containing high proportion of zinc are expected to produce considerable amount of zinc oxide which may or may not be mixed with other oxides e.g. tin, lead, iron, antimony, aluminium, manganese, etc. in varying amounts depending on the nature of the process adopted and the composition of scrap charge. Further treatment of oxide should, therefore, be a necessary adjunct to improve upon the economics of the processes except in cases where pure or almost pure zinc oxide is obtained.

Zinc oxide with small amounts of lead up to 0.05%can be used for manufacture of zinc oxide pigments. Lead compounds up to 15% can be tolerated in leaded zinc oxide paints. The zinc-rich oxide fumes, produced during refining of mixed bronze-brass scrap may contain 70-80% zinc, 1-8% lead and up to about 1% tin while the tin-rich oxide fumes may contain about 56% tin, 5-14% zinc and 14-28% lead.

A number of processes have been patented for treatment of mixed oxides working on the principle of differential volatilisation and extraction by leaching. The zinc-rich oxides at Zinnwerke Wilhelmoburg, Germany, were roasted with coke, soda ash and flourspar in a reverberatory or rotary furnace trapping the zinc oxide at the mouth of the furnace while molten lead-tin alloy remained in the furnace. The lead-tin alloy is further treated in a refining kettle with caustic soda, sulphur and aluminium to remove residual zinc and part of arsenic, copper and antimony, together with residual arsenic respectively. The refined alloy is used in the manufacture of tin-lead solder. In another patented method the mixed oxides, treated with 8% coke and pulped with water, were smelted under strongly reducing atmosphere. It was claimed that 99% of the zinc could be removed leaving a tin-lead alloy suitable for production of solder.

In the leaching method, the mixed oxides are leached with dilute hydrochloric or sulphuric acid when zinc, remaining in solution as chloride or sulphate, can be used for production of chemicals or extracted electrolytically. The residue can be treated with caustic soda to remove lead and tin oxide reduced in a reverberatory furnace and refined electrolytically. When antimony is present after extraction of zinc, the residue is dried and roasted at 480°C and leached with hot 16% sulphuric acid to remove copper and half of the antimony, which can be recovered. The residue from the second leach is mixed with 50% by weight of soda ash, roasted and leached with 10-15% sodium carbonate solution to remove the balance of antimony which can also be recovered. The residue from the third leach containing tin and lead is extracted as lead-tin alloy by smelting. These processes can be applied to treat tin as well as zinc-rich mixed oxides.

#### Conclusion

In conclusion, it is emphasized that reclamation of non-ferrous scrap is directed primarily to conserve scarce and expensive non-ferrous metals. The necessity, therefore, to get in the first instance the maximum from the raw materials utilised in the foundries should not be undermined. Another aspect which needs proper consideration is that jobbing foundries are not usually equipped with adequate facilities for reclamation work. Moreover, the trend in such foundries would be to

#### Bhat.acharyya : Reclamation of copper-base scrap and residues

concentrate more on the outturn of castings, their primary concern, than on the overall economics, that may accrue from conversion of all suitable grades of their own scrap arisings and utilising them as raw materials in the production of castings. It is, therefore, desirable to create adequate facilities and set up in such foundries for undertaking reclamation work as a regular measure. At times certain types of scrap arisings are converted into non-standard grades of castings from considerations of immediate benefit. Downgrading of valuable non-ferrous scrap in this manner is undesirable and should be discouraged.

#### Acknowledgement

The author's thanks are due to the Director General, Research Designs and Standards Organisation, for kind permission to present this paper.

#### References

- 1. Self-sufficiency in Indigenous Metals by V. Muthukrishnan et al., First Get-together of Research and Industry, December, 1965.
- 1965.
   Utilization of Metallurgical Waste on the Indian Railways— Non-ferrous Metals by K. C. Choudhuri and P. K. Munshi. Paper presented at the Symposium on Utilization of Metal-lurgical Waste at NML in March, 1964.
   Report by the Railway Board on Indian Railways for 1966-67.
   The Refining of Copper-base scrap, Dr. T. W. Farthing, Paper presented in the Symposium "The Effective Utilization of Copper" held in Calcutta, January, 1968.
   Ingot Manufacture. Metal Industry, Jan. 25, 1952-W. G. Mochrie.

- Mochrie. 6.
- Recovery of Copper from Scrap, Transactions of Indian Institute of Metals, 1951–D. S. Tandon and T. Banerjee. Metallurgical Treatment of Swarf by E. R. Thews, Metal 7.
- Metallurgical Treatment of Swarf by E. R. Thews, Metal Industry, Jan., 4, 1952. Dr F. M. Pinoff : Discussion in the Treatment of Swarf and Residues, Metal Industry, 11th March, 1955. W. S. Nelmes, et al. : Oxygen Jetting Secondary Copper, March, 1961, Journal of Metals. The Recovery of By-product Metals in the Smelting of Copper Alloy Scrap by Marjorie E. Whitaker, Oct., 1949.
- 9
- 10.

<ul> <li>U.K.+</li> <li>U.K.+</li> <li>Scrap : Beech, Brass, Heavy Yellow : pieces inclusheet, pipe and rod scrap in crucible of various size pieces. It may contain up to y also connect ings and rod scrap in crucible size pieces. It must be free from material. It must be free from any oldered parternovable condenser tubes and iron and permissible other foreign material.</li> <li>brass turn- Grass 33 Brass, turnings : Free from Al, Mn and any other admixture. Iron and mois-ture content should not exceed also.</li> <li>nor bronze</li> <li>nor bronze</li> </ul>	66		APPENDIX	I XIC	
<ul> <li>Badli, Heavy Brass Scrap : It shall consist of pieces including utensils, heavy sheet, pipe and rod cutings of various and rod contrings of various prass alloys. It may also con- trin 15% nickel-plated, tinned, prass alloys. It may also con- trin 15% of plated and soldered at of the soldered par- conceplated and soldered par- condenser tubes and iron any with difficulty is permissible with difficulty is permissible off.</li> <li>Beas 67 Yellow brass turn- free from Al, Mn and and and and off.</li> <li>Beas 67 Yellow brass turn- free from Al, Mn and and off.</li> <li>Beas 67 Yellow brass turn- free from Al, Mn and and off.</li> <li>Beas 67 Yellow brass turn- free from Al, Mn and and off.</li> <li>Brass, turnings : prose astings contain- free from Al, Mn and any other foreign material.</li> <li>Brass, turnings : free from Al, Mn and and other foreign material.</li> <li>Brass, turnings : free from Al, Mn and and other foreign material.</li> <li>Brass, turnings : free from Al, Mn and and other foreign material.</li> <li>Brass, turnings : free from Al, Mn and any other admixture. Iron and mois- ture content should not exceed 3%.</li> <li>Bhind 7.1 Phosphor bronze scrap : Phos. Bronze castings contain- ing a minimum of 4%. Sn and maximum Po 40°.5%.</li> </ul>		Railways	I.S.I.*	U.K.†	U.S.‡
<ul> <li>Beas 6.7 Yellow brass turn- ings and borings: Free from Al, Mn and any Free from Al, Mn and any other admixture. Iron and mois- ture content should not exceed Mn, babit metal.</li> <li>Bhind 7.1 Phosphor bronze scrap : Phos. bronze castings contain- ing a minimum of 4% Sn and maximum Pb content of all the The total content of all the</li> </ul>		NFB 1. Brass Lump Scrap : Comprising flanges, tubings, tube cuttings, lamp holders, utensils, etc., and brazing metal scrap.	Badli, Heavy Brass Scrap : It shall consist of pieces inclu- ding utensils, heavy sheet, pipe and rod cuttings of various brass alloys. It may also con- tain 15% nickel-plated, tinned, chrome-plated and soldered par- ts. Iron which is removable with difficulty is permissible up to a maximum of 1%. Lead attachments shall be sweated off.	Beech, Brass, Heavy Yellow : May consist of heavy brass cast- ings and rod scrap in crucible size pieces. It may contain up to 15% of plated and soldered material. It must be free from Mn, Al, Si and Ni mixtures, condenser tubes and iron and other foreign material.	Honey, Yellow, brass scrap: Shall consist of brass castings rolled bars, including plated brass. Must be free from manga- nese bronze, aluminium bronze, unsweated radiators or radiator parts, iron, excessively dirty and corroded materials. Ivory : Yellow brass castings-Shall con- sist of yellow brass castings in crucible shape, no piece to mea- sure more than 12 <sup>m</sup> over any 1 part, and shall be free of brass forgings, silicon bronze, alumi- nium bronze and Mn bronze and not to contain more than 15% nickel-plated material.
Bhind 7.1 Phosphor broscrap : scrap : Phos. bronze castings conting a minimum of 4% Sn maximum Pb content of 0. The total content of all		NFB 2. Brass borings : Turnings, fittings, shavings of brass (copper-zinc alloy) with or without any admixture.	brass t mixture u ee from	Grass 33 Brass, turnings : Free from Al, Mn and any other admixture. Iron and mois- ture content should not exceed 3%.	Nomad 33, Yellow brass tur- nings: Free from Al, Mn, and com- position turnings, not to contain over 3% free iron, oil or other admixture free from grindings and babbits.
		NFB 3. Bronze Lump Phosphor bronze Cl. I : Broken, worn out and defective castings such as slide valves, liners and small bushes, axle box scrap if made in Cl. I.	Bhind 7.1 Phosphor bronze scrap : Phos. bronze castings contain- ing a minimum of 4% Sn and maximum Pb content of 0.5%. The total content of all the impurities shall not exceed one per cent.		1

\*Indian Standard 2006-1962 coding and classification for non-ferrous scrap metals and residues. †U.K. National Association of non-ferrous scrap metal merchants. ‡U.S. National Association of Secondary Material Industries.

Railways	I.S.I.*	U.K.†	U.S.‡
NFB 4. Bronze, Cl. II (Gun metal): Broken, worn out and defective castings, such as boiler moun- tings, etc.	Bijoli 7.2 Gun metal scrap : Valves, machinery, bearings and other machinery parts, inclu- ding misc. castings made of copper.	Crows 22, Gun metal : In crucible size pieces to be free from heavy materials, must be free from Fe.	Eland 12 High grade, low lead bronze solids.
NFB 5. Lead bronze Cl. III : Broken, worn out and defective castings such as grease lubri- cated axle boxes, crown bea- rings, etc.	Bulsar 7.6 High lead bronze : Min. Pb content of 9%.	1	Elias 14, High lead bronze solids and borings :
NFB 6. Lead bronze Cl. IV : Broken, worn out and defective castings such as connecting rod, bearings, etc.	1		1
NFB 7. Bronze, Cl. (Modified Cl. III) : C and W bearing shells and all other casting made out of this.	1	1	
NFB 8. Bronze borings quality 1 of phosphor bronze Cl. I.	. 1	I	I
NFB 9. Bronze borings quality 1 Cl. II.	1	Gulls 34, Gun metal borings : Should be free from grindings excessively leady material and Al, Mn and Si mixtures and commercially free form brass. Fe and moisture contents com- bined should not exceed 3%.	

-contd.	
-I XIQN	
APPE	

	U.S. <sup>‡</sup>	Elias 14. High lead bronze solids and borings. It is recom- mended that these materials be sold on sample or analysis.		ix- Drink 7Refinery brass shall contain a minimum of 61.3% of copper and maximum 5% iron igs. and to consist of brass and bronze mi- solids and turnings and alloyed cun contaminated scrap. ain Every 10Red brass composi- tion turnings shall consist of turnings from red brass comp. material and should be sold subject to sample or analysis.	
	U.K.†			Frogs 31Brass borings mix- ed : May consist of any kind of brass borings and turnings. They may be slightly contami- nated with aluminium and gun metal borings and may contain up to a maximum of 10% in all of Mn and Al. mixture borings. Iron and moisture contents combined should not exceed $S_{00}^{0}$ .	
VIGNITIV	*.1.1.1		]	Biral. 7.4 Mixed brass bronze turnings and borings with white metal.	Guntur 14–2. Bronze residues and skimmings : There are skimmings and resi- dues arising in the bronze foundry. These may contain 10–50% Cu, 2–5% Sn, with or without small quantities of other elements such as Zn, Ni, Al, Pb, etc. Concentrates shall not be included as they can- not be technically termed as met residue.
	Railways	NFB 10. Bronze borings qua- lity 1 : Lead bronze.	NFB 11. Bronze borings qua- lity 2.	NFB 12. Bronze borings qua- lity 3 : Comprising all types of bronze and brass borings mixed with white metal borings and ferrous drillings.	NFB 13. Foundry dross and foundry sweepings, etc. all types.

\*Indian Standard 2006-1962 coding and classification for non-ferrous scrap metals and residues. +U.K. National Association of non-ferrous scrap metal merchants -‡U.S. National Association of Secondary material Industries.

	T	;
	1	2
	ē	5
	ì	,
)	1	4
ì	*	9
ţ	1	1
Ş	-	1
ì	1	1
ī	+	j.
7	2	
ł	-	4
ļ	2	ŧ.
		4

Railways	I.S.I.*	U.K.†	U.S.‡
NFB 14. Manganese-bronze lump scrap.		Hares 35. Mn-Bronze castings : Should be free from Al-bronze, Si-bronze, Fe and any other foreign material.	Parch 39. Manganese bronze solidis : Shall have Cu content of not less than 55%, a Pb content of not more than 1% and shall be free from Al-bronze and Si- bronze.
NFB 15. Mn-bronze drillings.	1		
NFC 1. Copper arsenical lump scrap : (a) Fire box, plates, water space stays, etc.	Chanda 8:4. Fire box copper : Consists of fire boxes taken apart with the rivets knocked out.		
NFB 17 (b) Copper ingots.	Ι	-	
NFB 18 (c) Copper wire.	Cambay 8·1 No. 1 Copper wire : Clean, untinned, uncoated, un- alloyed copper wire, cables, heavy field wire and heavy armature wire of size not less than 1·6 mm. It shall be free from burnt copper wire which is brittle and free from any foreign matter.	Colts 29. Copper wire No. 1 : Clean untinned H.C. copper wire not thinner than 22 gauge, free from hard wire, brittle burnt wire and iron and free from any other foreign matter.	Berry 2. No. 1. Copper wire : Clearn, untinned, uncoated, un- alloyed copper wire and cable, not smaller than No. 16 B and S wire gauge, free from burnt wire which is brittle. Hydrauli- cally briquetted copper subject to agreement.
*Indian Standard 2006-1962 ( +U.K. National Association c ‡U.S. National Association o	*Indian Standard 2006-1962 coding and classification for non-ferrous scrap metals and residues. +U.K. National Association of non-ferrous scrap metal merchants. ‡U.S. National Association of Secondary material Industries.	rrous scrap metals and residues. its.	

	U.S.‡	Berch 3. No. 2 Copper wire : Misc. unalloyed copper wire having a nominal 96% Cu con- tent (min. 94%) as determined by electrolytic assay. Should be free from following : Excessively leaded, tinned, soldered copper wire, brass and bronze wire, excessive oil content, iron and non-metallics, copper wire from burning, containing insulation a hair wire, burnt wire which is brittle and should be reasona- bly free from ash hydraulically briquetted copper subject to agreement.		f
K I—contd.	U.K.+	Corgi 21. Copper wire No. 2. Burnt tinned wire and may contain a percentage of un- burnt, tinned and soldered wire. It must be free from hair wire, vat wire, burnt wire which is brittle and iron.		
APPENDIX	I.S.I.*	Chamak 8.2. No. 2 Copper wire : It shall consist of misc. clean copper wire which may contain a max. of 15% of tin coated, lead coated, solder coated ena- melled wire and copper wire with soldered ends free from hair wire thinner than 0.10 Mn or burnt copper wire.	Chota 8.8. Copper turnings and boring : Clean Cu-turnings and borings free from foreign matter. Oil and moisture up to a max. of 1% is permissible if over 3% corresponding deduction in wei- ght should be made.	l,
	Railways	NFB 18 (c) Copper wire-contd.	NFB 19. Copper boring and turning.	NFB 20. Copper electrolytic pure.

\*Indian Standard 2006-1962 coding and classification for non-ferrous scrap metals and residues. +U.K. National Association of non-ferrous scrap metal merchants. ‡U.S. National Association of Secondary material Industries.

Bhattacharyya : Reclamation of copper-base scrap and residues

# Discussions

Mr L. N. Misra (Khetri Copper Project): The author has very clearly described the steps in reclaiming nonferrous metals from scrap. We would like to have some more details on the reclamation of metallics from the fines. Reverberatory melting is not recommended because of high fuel losses. If the fines are melted in crucible or hearth furnaces, the large surface area and consequently the large bulk brings down the capacity of melting.

What is the opinion of the author on the chemical dissolution of the metallic fines and their reclamation either as metallic salts or as metals through chemical or electrochemical means.

Mr A. K. Bhattacharyya (Author) : Fines, rich in metallics which do not require much refining, can be conveniently melted in crucibles. Metallics from fines requiring substantial refining may be briquetted and melted in a reverberatory or hearth type furnace. Suitable fluxes are sometimes incorporated in the briquettes to aid the refining process. In the reclamation of metallics from residues, the usual procedure is crushing, concentrating and screening. Usually, sieving through 100 mesh should be adequate for economic recovery of most of the metallics. Though more metallics can be recovered by using finer sieves, it has to be considered that such procedures will not only involve more time and labour, but also may not result in higher yield as fines above 150 mesh will probably be returned in the residues through skimmings, slag, etc. without adding to the recovery. The price of metal in the fines, of course, is an important factor deserving due consideration while selecting a reclamation procedure.

It is true that crucible melting in case of fines or finely divided scrap brings down the melting capacity due to increased volume per unit weight of charge. On the other hand, it is to be considered that oxidation losses, due to flame coming in contact with the charge,

will be high in reverberatory melting as such losses increase directly with the surface area per unit weight of charge. Another important factor deserving due consideration is contamination of the refractory lining of the hearth during melting. Unless, therefore, long runs of similar type of scrap are melted, crucible melting may be preferred to flexibility.

Chemical dissolution processes are in vogue for recovery of by-product metals from copper-base scrap, such as acid leaching of mixed oxide fumes of zinc, lead and tin, obtained as by-products in the recovery of bronze and brass scrap, liquid extraction of non-ferrous metals by organic extractants and complexing agents, etc.

We have not done any work in melting of cement copper. It is, however, considered that briquetting of cement copper and refining in hearth type of furnaces may be an economic proposition. Where small quantities are involved, crucible melting may yield satisfactory economics.

Mr D. J. Hughes, (UNESCO Expert, Regional Institute of Technology, Jamshedpur) : In view of the well known deleterious effect of bismuth in copper what steps are taken in your reclamation and recovery processes to eliminate it?

After reclamation and purification what are the possible uses for the metal? Presumably, the degree of refining is not sufficient to permit conductivity applications of the metal.

Mr A. K. Bhattacharyya (Author): Presence of bismuth in reclaimed scrap has not been reported to be a problem in the railway foundries. No special steps are, therefore, taken to eliminate bismuth while reclaiming copperbase scrap for use in our foundries.

The reclaimed copper-base scrap is utilised in railway foundries mostly for production of bronze castings.