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# Solid waste management in non-ferrous industries in India

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#### Abstract

This paper highlights the production capacity, type and quantity of solid wastes generated, their chemical composition and treatment/disposal options for the Indian aluminium, copper lead and zinc industries. Red mud, spent pot lining (SPL), fly ash from aluminium industries; scrap, slag, dross, reverts, slime, flue dust, mill scales, sludge etc. from copper industries; zinc tailing, slag, leach residue, jarosite residue, β-cake, etc. from zinc industries and BF slag, flue dust, ISF slag etc. from lead industries are the major solid waste generated from the process. Common practices of waste management in these industries are through recycling and recovering the metal values and dumping. Owing to the presence of the toxic elements in some of the solid wastes cause environmental degradation. Stringent pollution control rules are being enacted and implemented as a result of which all the metal producing industries in organised sector are now taking care of the environment and waste management related problems, but pollution from unorganized lead units are the major cause of concern. Permissible limits of toxic constituents in zinc based secondaries and threshold zinc concentration for both indigenous and imported raw material were worked out at National Metallurgical Laboratory (NML) and based on these results a recommendation to MOEF, Government of India was made to specify the permissible limits for the import of zinc secondaries. An overview of the attempts made to recycle/recover metal values and production of value added products, at NML are also mentioned in the text. © 2003 Published by Elsevier B.V.

Keywords: Pollution measures; Non-ferrous metal; Aluminium; Copper; Zinc; Lead

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#### 1. Introduction

Non-ferrous metals besides gold, silver and platinum are somewhat toxic to living organism. It is therefore important that all the metallurgical industries not only take care of the process of manufacture but also safe disposal of the pollutants generated in the form of solids, liquids or gaseous wastes. Metallurgical industries generate vast quantities of solid wastes such as slag, ash, sludge, dross, grindings, turnings, clippings, residues and secondaries. During the last few decades rapid industrialization has led to many fold decline in the quality of environment. Some of the solid wastes produced during metal extraction are hazardous in nature, since they contaminate the surface and ground water through the leachate generated at the dump-sites, which is a risk to the life of the living organism. Effects of pollution due to the toxic constituents of the above leachate, are usually noticed in the long run. It is for this reason that the industries are not much concerned about the solid metallic wastes that are invariably thrown and dumped unsystematically during metal production. The type of metallic waste generated, depends on the quality of raw materials used, the process and the treatment methods. Irrespective of the physical forms such as solid, liquid and gas, the wastes generated are eventually of two types: hazardous and nonhazardous. Amongst the heavy and toxic metals, arsenic, cadmium, chromium, nickel, lead, copper, mercury and zinc are considered deleterious to the environment, when their concentrations are more than the stipulated limits. The major environmental degradation is caused by copper, lead and zinc industries, often using imported zinc ash/residue, dross, skimming, lead scrap etc. It has therefore become a major issue enforcing agencies to take policy decisions regarding import of such wastes and identifying the industries having environmentally sound technology.

As the leachate generating from the dumping of the hazardous wastes contaminates the environment, efforts must be directed towards not only effectively monitoring and managing the environment but also developing and applying viable and acceptable ecofriendly processes and waste handling/management technologies to cater to the pollution free environmental control of even the small and medium scale industries.

With a view to assessing the environmental problems associated with hazardous constituents of these materials, National Metallurgical Laboratory (NML) has developed a valuable database information bank on Indian ferrous and non-ferrous industries detailing quantity and composition of the various solid wastes/secondaries generated, processing options for such materials and their management. This paper deals with an overview of the non-ferrous process industries (data on all the major and those minor industries which co-operated to give the information) and their attempts to save the environment from degradation. The attempts for the development of Process for the utilization of various wastes of non-ferrous industries, at NML are also highlighted.

### 2. Aluminium industries

Bayer's Process is the only process adopted world wide for the production of aluminum in which substantial amount of red mud is generated. Production of 1 t of alumina is accompanied by generation of about 1.0–1.5 t of red mud. It is more than a century that the

industry has not come up with any viable alternate economic method to treat bauxite for production of aluminum, which does not generate red mud. Indian alumina plants have 1.692 million tons of annual capacity (Chandwani et al., 1997; Kumar et al., 1998) with metal production of 6,00,000 t per year and generate about 2 million tons of red mud every year.

The major constituents of red mud are the oxides of Fe, Al, Si, Ti, Na and Ca along with a large number of minor constituents. The alumina, silica and soda account for about 40% of the total red mud and rest are mostly in the form of iron and titanium oxides. The chemical composition of the red mud, collected for Indian industries are revealed in Table 1.

Besides the red mud, other two major solid wastes generated in the aluminum industries are spent pot lining (SPL) and fly ash (Table 2). The electrolytic cell consists of a carbonaceous material with an outer lining of firebrick or alumina refractory lining. During the course of electrolysis this lining is impregnated with sufficient levels of sodium (12–18%), fluoride (12–18%) and a small amount of cyanide (0.1–0.3%). It is this lining termed as spent pot lining, which is dugout for disposal. About 20–40 kg of SPL is generated per tonne of aluminum produced.

## 2.1. Waste treatment/disposal in aluminum industries

Red mud disposal causes seepage of the alkaline liquid into groundwater, which might contaminate industrial, domestic, and agricultural water supplies; spillage from damaged pipelines or from retaining-dyke failure, reduction in the availability of arable land, requirement of huge area (Prasad and Subramanian, 1997) (viz. 2 million square kilometer per annum) dust pollution in arid regions, aesthetic impacts, etc. are the other problems prevalent in these units.

With the growing concern of environmental protection as well as land conservation, a systematic effort has been made to modify and improve upon the methods of disposal. The details of the red mud disposal practices (Prasad et al., 1996) at the Indian alumina plants are

| Table 1   |
|---|
| Chemical composition (%) of red mud generated at different plants (Agrawal, 1999; Kumar et al., 1998; Seth, |
| 1998; Senapati, 1998)   |

| Constituents                   | NALCO<br>(Seth,<br>1998) | HINDALCO<br>(Agrawal,<br>1999) | MALCO<br>(Kumar<br>et al., 1998) | BALCO<br>(Kumar<br>et al., 1998) | INDAL, Muri<br>(Senapati,<br>1998) | INDAL, Balgaum<br>(Kumar et al.,<br>1998) |
|--------------------------------|--------------------------|--------------------------------|----------------------------------|----------------------------------|------------------------------------|---|
| Al <sub>2</sub> O <sub>3</sub> | 15.0                     | 17–22.4                        | 14.0-                            | 18.0–20.0                        | 24.0–26.0                          | 18.0–20.0                                 |
| $Fe_2O_3$                      | 62.78                    | 25.6-33.2                      | 18.0                             | 27.0-29.0                        | 36.0-38                            | 40.0-50.0                                 |
| TiO <sub>2</sub>               | 3.77                     | 15.6-16.5                      | 50.0-                            | 16.0-18.0                        | 16.0-20.0                          | 8.0-11.0                                  |
| $SiO_2$                        | 6.55                     | 6.9-8.25                       | 56.0                             | 6.0 - 8.0                        | 5.0-6.0                            | 5.0-7.0                                   |
| CaO                            | 0.23                     | 5.6-14.6                       | 2.0-4.0                          | 6.0 - 12.0                       | 0.8 - 1.0                          | 1.0-3.0                                   |
| Na <sub>2</sub> O              | 4.88                     | 3.9-5.8                        | 6.0 – 9.0                        | 4.0 – 6.0                        | 3.0-3.5                            | 3.0-4.0                                   |
| Mn                             | 1.1                      | _                              | _                                | _                                | _                                  | _   |
| $P_2O_5$                       | 0.67                     | _                              | 1.0-2.0                          | _                                | _                                  | _   |
| $V_2O_5$                       | 0.38                     | _                              | _                                | _                                | _                                  | _   |
| $Gd_2O_3$                      | 0.01                     | _                              | _                                | _                                | _                                  | _   |
| LOI                            | 9.50                     | 8.5–12.6                       | -                                | 12.60                            | _                                  | 10.0                                      |

| Table 2<br>Chemica | l composition (%) of | f fly ash and spent pot lining | g (Agrawal, 1999; Seth, 1998) |
|--------------------|----------------------|--------------------------------|-------------------------------|
| Serial             | Name of the          | Spent pot lining               | Fly ash                       |

| Serial<br>number | Name of the plant                                      | Spent pot lining   | Fly ash   |
|------------------|--|--|---|
| 1                | HINDALCO,<br>Renukoot                                  | Al <sub>2</sub> O <sub>3</sub> : 19.0–24.0, SiO <sub>2</sub> : 10.0–13.0<br>Fe <sub>2</sub> O <sub>3</sub> : 0.5–0.8, Na <sub>2</sub> O: 27.0–34.0,<br>CaF <sub>2</sub> : 2.0–4.0, fluoride (T):<br>11.0–14.0  | Al <sub>2</sub> O <sub>3</sub> : 13.0–35.0, SiO <sub>2</sub> : 53.0–71.0<br>Fe <sub>2</sub> O <sub>3</sub> : 3.5–12.0, TiO <sub>2</sub> : 0.5–2.0 CaO:<br>0.6–6.0, Na <sub>2</sub> O/K <sub>2</sub> O: 0.12–5.0 P <sub>2</sub> O <sub>5</sub> :<br>0.3, MgO: 0.28–3.24, SO <sub>3</sub> : 0.005–1.1 |
| 2                | NALCO  | SPL: middle layer Al <sub>2</sub> O <sub>3</sub> : 1.88,<br>SiO <sub>2</sub> : 1.56, Fe <sub>2</sub> O <sub>3</sub> : 0.53, Na <sub>2</sub> O:<br>19.22, fluoride: 10.88, CN: traces<br>0.3, LOI (C): 67.61<br>SPL: bottom layer Al <sub>2</sub> O <sub>3</sub> : 3.2, SiO <sub>2</sub> :<br>65.81, Fe <sub>2</sub> O <sub>3</sub> : 1.18, fluoride: 2.5,<br>CN: traces 0.08, Na <sub>2</sub> O: 1.24, LOI | Al <sub>2</sub> O <sub>3</sub> : 28.23, SiO <sub>2</sub> : 59.72 Fe <sub>2</sub> O <sub>3</sub> : 5.37, TiO <sub>2</sub> : 2.01, CaO: 1.39, Na <sub>2</sub> O: 1.23, P <sub>2</sub> O <sub>5</sub> : 0.93, MgO: 0.83, SO <sub>3</sub> : 0.21, MnO: 0.08   |
| 3                | General analysis<br>for other Indian<br>aluminum units | (C): 0.54<br>Al <sub>2</sub> O <sub>3</sub> : 15–25, SiO <sub>2</sub> : 9–13, Fe <sub>2</sub> O <sub>3</sub> :<br>0.4–0.9, fluoride: 12–20, CN: traces<br>0.08, LOI (C): 40–55, CaF <sub>2</sub> :<br>0.123–1.23   |   |

summarised in Table 3. Many plants in recent times are practising dry staking disposal of red mud which requires much less land and promotes consolidation and hardening of red mud, consequently resulting in stable and safer deposal. On account of damage to aquatic/marine life disposal into sea or river streams is not favoured. Out of 84 alumina plants all over the world, only seven are still practising the sea disposal in a planned manner because of scarcity of land.

Because of the high alkalinity, this red mud is usually not suitable for cement production or metal extraction. However, it is used for making tiles, building material, doors and windows, road construction, pig iron production etc. Since red mud contains appreciable amount of iron oxide (25–50%, Table 1) depending on the chemical and mineralogical make up of bauxite and treatment process, attempts have been made to recover iron (Kumar et al., 1998; Prasad et al., 1985; Thakur and Das, 2003), Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> etc. from it. In this context a know-how for the recovery of iron, vanadium, chromium and aluminium oxide from red mud has been developed at Regional Research Laboratory (RRL), Bhubaneswar (Bhattacharaya et al., 1987; CSIR News, 1996; Prasad et al., 1985). National Metallurgical Laboratory, Jamshedpur had also evaluated the technical feasibility of the process of extracting Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> from the red mud of Muri by soda lime sintered process (Prasad et al., 1985). Prasad et al. (1985) have explored the production of ferrotitanium to utilise both iron and titanium values from Indian red mud. Recent studies at NML has focused primarily on the utilisation of red mud (Kumar et al., 1998) for iron and other metal values recovery by applying Elgai process (Vhatkar, 1990) and on the sintering of iron ore, using the red mud of National Aluminium Company (NALCO), Bhubneshwar, which contains about 50-60% of Fe<sub>2</sub>O<sub>3</sub>. The process involves alkali roasting of red mud in presence of carbon at 750–800 °C, leaching of aluminium values for alumina recovery and separating the iron values from the residue as magnetic fraction and titania as the non magnetic fraction.

Table 3
Red mud disposal practices at the Indian alumina plants

| Serial<br>number | Name of the plant     | Plant capacity (t) | Red mud (t/t) of alumina | Dumping procedure   |
|------------------|-----------------------|--------------------|--------------------------|---|
| 1                | INDAL, Muri           | 72,000             | 1.35–1.45                | This refinary adopted the closed cycle (wet slurry) disposal system (CCD). The disposal ponds have not been provided with any liner.  |
| 2                | INDAL,<br>Belgaum     | 2,20,000           | 1.16                     | The plant switched over to dry disposal mode from wet slurry disposal mode in 1985. The mud after clarification passes through six stage counter current washing and after filtration (65% solids), it is disposed off by dumpers at the pond site. The dry portion of the pond is covered with a 15 cm black cotton soil for promoting green vegetation. |
| 3                | HINDALCO,<br>Renukoot | 3,50,000           | 1.4                      | Traditional CCD method of impoundment was used. In late 1979 dry disposal method was implemented. After five stages counter current washing the solid is filtered (70% solids) and disposed off into the pond.  |
| 4                | BALCO,<br>Korba       | 2,00,000           | 1.3                      | Residue after settling, counter currently washed in four stages and filtered. The filtered cake is repulped with the pond returned water and dumped in the pond. Uses modified CCD system of disposal. The dykes of the currently used pond have stone masonry and well protected polythene liner and clay layer.   |
| 5                | NALCO,<br>Damonjodi   | 8,00,000           | 1.2                      | A modified CCD method is used for disposal. Subjected to six stage counter current washing by pond returned water (0.5 g/l Na <sub>2</sub> O) and condensate from the evaporators. The washed red mud is repulped and sent to disposal sites. The bottom and sides of the pond are covered by impervious and semi pervious clay with base filters.        |

CCD: closed cycle disposal; MCCD: modified CCD; DS: dry stacking.

Spent pot lining and fly ash are mostly stored in the secured landfill. Indian Aluminium Company (INDAL, Muri), plants were the first to treat spent pot lining (SPL) in an ecofriendly manner and store it. The newer plants like NALCO also treats the SPL with bleaching powder and burnt lime and store in the premises. Other aluminum plants also store the SPL in the designated areas. Some attempts have been made world over to use spent pot lining for the recovery of valuables like fluorides (mainly as cryolite), caustic, and carbon for reuse in aluminium smelters as carbon blocks and ramming pastes and also in the arc furnace steel melting shops. At present CIS Countries in USSR are using this material (SPL) for reduction of coke/fluxes/fuel in the electric arc furnace process for iron making. This particular option needs to be tried in India for such purposes (Deshpande, 1998).

Fluoride in aluminium industries contaminates the environment (Ramchandran and Agrawal, 1997) through primary and secondary emissions (1–6 kg/t) and SPL (4–8 kg/t) besides wastewater. Scrubbing process and SPL treatment recovers a major part of fluoride and it is therefore essential to monitor the wastewater to check the fluoride contamination.

Fly ash is generated in the alumina plant (where high pressure steam is required for high temperature pressure/Bayer digestion process) and in captive power station located near

aluminium smelters. The installed power generation plant including those from aluminium industries with a capacity of about 70,000 MW would generate about 100 Mt of fly ash per annum. The space required for dumping 100 million tonnes of fly ash would be fairly large (1 km²/5 Mt of fly ash) with a water requirement of about 1200 Mt (Rao, 1997). Disposal requires enormous amounts of power to pump out the slurry while causing a serious environmental problem. Therefore, the economic utilization of fly ash in different ways like cement making, brick making, aggregate making, soil conditioner, and even for precious metal recovery, needs an immediate effort to mitigate the disposal problem and environmental hazards. Unlike other countries, only 5–10% of fly ash produced is used in India while the rest is disposed off as dumped waste. The chemical composition of the fly ash generated by a few major aluminium plants is given in Table 2. By the end of this century India will be generating about 130 Mt fly ash creating a major problem to the nation and hence the producers should organise a systematic planned development of scheme for the useful utilization of this resource.

Other wastes like scrubber sludge, which is produced during the treatment of exhaust gases from pot using wet scrubber, contains calcium fluoride, aluminium and lime. This sludge can be converted to a product called ALUSPAR-70, which is a substitute to metallurgical grade compound used in alloy steel refining process. At Hirakud aluminium smelter (INDAL), two pits were constructed as per the design of National Environmental and Engineering Research Institute (NEERI), Nagpur, for disposal of scrubber sludge and ETP sludge from effluent treatment plant containing substantial quantities of copper, tin and lead.

## 3. Copper industries

Copper as a metal provides limited scope for environmental pollution, but the waste generated by the copper based industries with various toxic elements can pollute the environment. Copper mining, smelting and refining activities are often associated with the generation of a large quantity of wastes. Overburden, mine tailings, sediments from concentrator plants and scrap, slag, dross, reverts, slime, flue dust, mill scales, sludge etc. from the process are the major sources of pollution unless handled and treated suitably.

The primary copper production by Hindustan Copper Limited from two units is 46,500 t per year (Indian Copper Complex (ICC) 16,500 t per year and Khetri Copper Complex (KCC) 30,000 t per year). The newer plants namely Indogulf-Birla Copper (capacity 1,00,000 t per year), sterlite (capacity 1,00,000 t per year) and SWIL (capacity 50,000 t per year) have also entered in the copper production from imported concentrates/secondaries. The details of the waste generated in some of the Indian industries, their chemical composition treatment and disposal methods are discussed in Table 4. Copper is consumed both as refined copper and as direct melt scrap in brass mills, wire rod mills, chemical plants and other miscellaneous manufacturing units. Recycle value of copper is the highest and is well above 90% of the primary metal produced. Nearly 40% of the total copper usage in the world is from secondary sources. Energy consumption and cost of production of a secondary metal is only a fraction of that of primary metal. The bulk of copper sulphate and copper chemicals in India are produced by small-scale units mainly from foundry dross, ash, scales, floor sweepings etc.

| Table 4<br>Details o | Table 4<br>Details of waste generated in sor | ne of the Indian coppe          | in some of the Indian copper industries and their treatment and disposal methods  |   |
|----------------------|--|---------------------------------|---|---|
| Serial<br>number     | Name of the plant                            | Type of waste                   | Chemical composition (%)  | Treatment/disposal method   |
| -                    | Hindustan Copper<br>Ltd. ICC, Ghatsila       | Converter slag                  | Cu: 1.8, Zn: 0.13, Ni: 0.87, Fe: 0.83, Co: 0.49, Mn: 0.03, S: 0.36, C: 0.23   | Recycled back to the plant  |
|                      |  | Anode slag                      | Cu. 35-45, Ni: 10-15, Zn: 0.02, Fe: 20-25, SiO <sub>2</sub> : 7-10, CaO: Goes for copper and nickel recovery 3.92, Al <sub>2</sub> O <sub>4</sub> : 3.3, Co: 0.3, Pb: 0.018, Te: 0.076, Bi: 0.018 | Goes for copper and nickel recovery   |
|                      |  | Anode slime                     | Cu: 12.3, Ni: 36.8, Se: 10.5, Te: 3.4, Ag: 1.5, Au: 0.0064, Pt: 0.015, Be: 0.015, Sb: 0.01, As 0.036, Pb: 0.16, SiO <sub>2</sub> : 4.0  | Processed for precious metal recovery   |
|                      |  | Dump slag                       | Cu: 0.68, Ni: 0.05, Co: 0.22, Fe: 47, Mn: 0.03, Zn: 0.05, S: 1.47, C: 0.16  |   |
|                      |  |                                 | Cu: 1.8–2.4, Fe: 40–42, Co: 0.18–.2   | Dumped near the plant along the river bank                                      |
| 2                    | Hindustan Copper<br>Ltd. KCC, Rajasthan      | Converter slag                  | ı   | Totally recycled back to the process.   |
|                      |  | Anode slag                      | 1   | I   |
|                      |  | Anode slime<br>Dump slao        | Cu: 0.06, Fe: 44, Ni: 0.06, Co: 0.13, Te: 0.014, SiO <sub>2</sub> : 28  | Exported for copper recovery Dumped after conner flotation                      |
| 3                    | Indo gulf (Birla                             | Granulated slag                 | Cu: 0.7, Fe: 47.8, SiO <sub>2</sub> : 29.9  | Utilised as a sand blasting, abrasive material                                  |
|                      | Copper), Gujrat                              |                                 |   | and rest dumped near the plant  |
|                      |  | Cu-arsenide                     | Cu: 65, As: 20, Sb: 1.0, Bi: 0.9  | Recovery of Cu and As is being explored.  |
|                      |  | Phosphogypsum                   | CaO: 31, P <sub>2</sub> O <sub>5</sub> : 1.0, F: 1.0, SiO <sub>2</sub> : 1.0, organic: 1.0,   | Yard has been designed for disposal   |
|                      |  | Fly ash/bottom ash              | Ash LOI: $1-16$ , SiO <sub>2</sub> : $40-64$ , Al <sub>2</sub> O <sub>3</sub> : $15-30$ , Fe <sub>2</sub> O <sub>3</sub> : $3-10$ ,   | Usage in cement and bricks industries are                                       |
|                      |  | and ETP waste                   | CaO: 1-6 ETP CaSO <sub>4</sub> : 72.9, Cu: 0.17, Ni: 0.95, Fe: 0.15   | being explored  |
| 4                    | Sterlite Industries<br>India Limited         | Granulated slag                 | Cu: 0.523, Co: 5.57, Ni: 0.58, Pb: 10.85, Fe: 42.83, SiO <sub>2</sub> : 30.12, Al <sub>2</sub> O <sub>3</sub> : 2.22  | Being dumped near the plant   |
|                      |  | Slow cooled slag                | Cu: 0.23, Co: 2.3, Ni: 0.37, Pb: 5.17, Fe: 36.89, SiO <sub>2</sub> : 30.91  | Being dumped near the plant   |
| 5                    | SWIL Ltd., Gujrat                            | Kaldo vitreous slag             | Cu: 0.44, Zn: 1.6, Pb: 0.32, Fe: 37.9, Si: 25.3, CaO: 3.9   | Sold to outside party for construction purpose                                  |
|                      |  | Converter vitreous              | Cu: 1.49, Zn: 3.3, Pb: 0.28, Fe: 55.0, SiO <sub>2</sub> : 24.8, Al <sub>2</sub> O <sub>3</sub> : 6.0  | Sold to outside party for construction purpose                                  |
|                      |  | slag                            |   |   |
|                      |  | Anode slime<br>Ventury scrubber | Ni: 23.0, Ag: 12.0, Sn: 2.4, Se: 1.2, Pb: 11.0, Cu: 1.0, As: 0.3<br>Cu: 1.0, Zn: 35.0, Pb: 1.5, Fe: 2.5, Si: 6.   | Sold for recovery of precious metal Sold to primary/secondary zinc manufacturer |
|                      |  | sludge                          |   |   |
|                      |  | SO <sub>2</sub> gypsum          | CaSO <sub>4</sub> : 90–94, CaCO <sub>3</sub> : 3–5  | Sold to cement industries   |
|                      |  | Evaporator rejects              | Na <sub>2</sub> SO <sub>4</sub> and I, Ca: traces   | To a centralised properly lined disposal sites                                  |

## 3.1. Waste treatment/disposal in copper industries

Copper based industrial waste suitable for copper recovery can broadly be classified on the basis of physical form, copper content, chemical nature, chemical composition and possible recovery process. Some of the more important copper bearing wastes amenable to copper recovery include the following (Vishwanathan, 1998).

- Metallic waste—heavy, medium and fine scrap.
- Compound waste—oxide scale.
- Oxidised bulk waste—slag, dross etc.
- Oxidised powder waste—anode slime, pickling sludge, floor dust, flue dust, spent catalyst, effluent sludge, mine tailings.
- Liquid waste—spent pickling liquors, spent electroplating solutions, industrial effluent, mine water etc.

Certain solid wastes from the copper industries are real assets and are the important secondaries. These are the useful sources of strategic metal such as nickel and cobalt and precious metals such as gold, silver, platinum etc. These secondaries are converter slag, anode slag, ETP sludge, anode slime etc.

The metallic wastes and certain other wastes like dross, reverts etc. are best recycled by pyrometallurgical process including melting, fire refining and electrorefining. Among the other waste except for high grade mill scale, all are mostly amenable to recovery by hydrometallurgical processing.

Anode slag consisting of nickel and copper at Indian Copper Complex (ICC), Ghatsila is used to recover copper and the residue is stored in the plant premises for possible nickel recovery (Biswas et al., 1998; Parvathisem, 1997). The converter slag is recycled back to the smelting furnace and precious metals like Ag and Au are recovered from the anode slime (70 t per year). The slag from ICC Ghatsila (60,000 t per year) is dumped near the smelter and the slag of Khetri Copper Complex, Khetrinagar (1,20,000) is subjected to copper recovery by flotation and the residual slag is dumped. An attempt made at NML shows (Ghosh et al., 2003) that cast iron of composition (%) Cu: 1.5-2.0, Si: 0.12-2.9, Mn: 0.03, P: 0.16, S: 0.7-2.0, C: 0.16-2.0, Fe: balance, can be produced from the dump slag of ICC, Ghatsila by smelting in an electric arc furnance. The metal (cast iron) could be used as wear resistant alloy for grinding media. Similar solid wastes (2.4 t/t of Cu of copper production) along with some important secondaries are also produced by Sterlite Industries India Ltd. (SIIL) at Tuticorin, which has an installed capacity of 1.0 lakh ton per year copper. NML, Jamshedpur has characterised and tested the possible utilisation of the dumped slag produced at SIIL (Premchand et. al., 2001). The slag was found nonhazardous and could be safely disposed off. The granulated slag was smelted to give the cast iron with the composition (%) Cu: 0.63, Si: 0.07, Mn: 0.01, P: 0.26, S: 0.41, C: 2.91, Fe: balance, which could be used for making grinding material.

The slag produced from Kaldo furnace (0.63 kg/kg of copper) of SWIL (Balachandran, 1999) consists of SiO<sub>2</sub> present in combined form as Fayalite i.e. 2FeO·SiO<sub>2</sub>. The slag is glassy in nature and as claimed by the company, it does not contain any leachable component. This slag is granulated and sold as abrasive. This inert slag can also be used for land filling, for making of road and in construction works like embankment for rivers etc. Converter

slag (0.36 t/t of copper) produced from SWIL and slag (2.4 t/t of copper) from Birla copper (Sharma, 1998) are granulated and some amount is sold out to the construction companies for road making, as abrasives for shot blasting media. Granulated slag from Birla copper is mostly dumped near the plant in designated area. Hence, its long-term effect on water pollution due to leachate generated may not be guaranteed unless it is proved non hazardous through toxicity characteristics leachate procedure (TCLP) test.

The ventury scrubber dust (0.27 t/t of copper) collected from Kaldo furnace (SWIL) contains zinc oxide and chloride, which is sold out to the manufacturer of zinc ingots/sulphate manufactures. Anode slime (420 t per year) produced at SWIL as a byproduct, is sold to the outside parties for recovery of precious metals like Au, Ag, Se, Te etc. It is processed by hydro-pyro metallurgical routes in some plants. Gypsum produced from SO<sub>2</sub> scrubbing and ETP unit is sold to cement industries.

The phosphogypsum produced (5.0 t/t of copper) by Birla Copper is being disposed off in a properly designed yard and its use as soil conditioner is yet to be established. Copper arsenide (0.004 t/t of copper) from the bleed stream is being considered for recovery of copper and arsenic and its use as wood preservative/insectiside is also explored.

The residues generated in copper primary smelters and also in the secondary plants from brass ash/dross are mostly stored within the plant premises. The liquid streams of these plants are processed in the effluent treatment plant and sludge generated is either processed/stored or sold to the respective metal recovery unit by pyro-hydrometallurgical techniques. The dust from the dust collecting system of several of the copper pyrometallurgical units are either stored for possible metal recovery or processed by hydrometallurgical routes.

#### 4. Zinc industries

The present smelting capacity for zinc in the country (Janardan, 1996) is 199,000 Mt of which HZL has 169,000 t (Debari: 59,000 Mt, Visakhapatnam: 40,000 MT, and Chanderia: 70,000 Mt) and Binani Industries Ltd. has 30,000 t. Production capacity of all the smelters associated with HZL is given in Table 5. HZL uses mainly indigenous zinc concentrate and occasionally importes from other countries while Binani Ltd. uses imported concentrates only. The total lead-zinc ore production capacity of HZL is 3.34 milliom TPA. Currently about 15% of zinc demand is met through secondary route against the world average of 32–35%. The secondary zinc producers recover zinc values from indigenous and imported zinc ash/skimmings/dross and play a vital role in bridging the gap between demand and supply for zinc. The numbers of secondary units is growing steadily and have reached to about 40, most of which are facing the problem of survival due to the recent ban on import of zinc secondaries.

All zinc wastes containing zinc have been categorised as hazardous waste under the Basel convention. Some selected dross, zinc scrap and skimmings are in green list of waste and zinc ash happens to be in amber list. The European union has placed all zinc containing wastes in the list of hazardous wastes. Because of the likely contaminants present in the zinc skimmings, a product of galvanizing operation, they have been placed under the categories of wastes for which the level of contamination is essential to quantify. The residue generated

| Serial number | Smelter                                 | Products       | Annual capacity (MT) |
|---------------|---|----------------|----------------------|
| 1             | Debari zinc smelter, Rajasthan          | ZINC-HG        | 59,000               |
|               |   | Sulphuric acid | 87,000               |
|               |   | Cadmium        | 250                  |
| 2             | Vizag zinc smelter, Visakhapatnam,      | ZINC-HG        | 40,000               |
|               | Andhra Pradesh                          | Sulphuric acid | 60,000               |
|               |   | Cadmium        | 115                  |
| 3             | Tundoo lead smelter, Jharkhand          | Lead           | 8000                 |
|               |   | Silver         | 12                   |
| 4             | Chanderiya lead-zinc smelter, Rajasthan | Zinc-SHG-PW    | 35,000               |
|               |   |                | 35,000               |
|               |   | Lead           | 35,000               |
|               |   | Cadmium        | 375                  |
|               |   | Sulphuric acid | 176,000              |
|               |   | Silver         | 74                   |
|               |   | Copper cathode | 2100                 |

Table 5
The production capacities of the smelters of HZL

from these materials by secondary units may have hazardous character depending on the concentration of the toxic constituents.

# 4.1. Waste treatment/disposal practices in zinc industries

The details of waste generated, their quantity, composition and treatment/disposal practices of some of the major zinc plants are incorporated in Table 6. At Binani zinc smelter (Thomas, 1998), the jarosite residue generated is pumped out and safely stored inside the company premises in a large pond of 1,40,000 M<sup>3</sup> (Seth, 1998) capacity. The residue contains toxic constituents in good amount like 3-5% Zn, 8-10% Pb, and 40-50% SO<sub>4</sub>. Ground water monitoring is periodically conducted from the tube wells installed around the ponds. Steps have been initiated for the construction of new jarosite ponds by conducting rapid environmental impact assessment (REIA). Based on the recommendation submitted by the public hearing panel, the government of Kerela notified the site for construction of jarosite pond. The design of the proposed pond is as per the guidelines of United States Environmental Protection Agency (USEPA) and Ministry of Environment and Forest (MoEF) for secure landfills. The pond design is based on geochemical investigations and compatibility studies with the waste. The pond is lined on all the sides and bottom with two layers of LDPE sheets of 250 µm thickness, heat sealed and protected by burnt clay bricks. The primary and secondary cake leach residues are also stored inside company premises in a covered shed provided with acid proof bricks at the bottom and disposed by way of sales.

HZL has been in forefront for adopting appropriate pollution control and environmental protection measures in all its operations. Environment impact assessments are undertaken for new projects to formulate Environment Management Plans for mitigating any possible environmental impacts.

The environmental measures at mining units of HZL include provision for dust suppression and collection system, disposal of beneficiation plant tailing into tailing ponds,

Table 6
Details of waste generated and treatment/disposal practices in zinc plant

| Serial<br>number | Name of the industry  | Waste generated: quantity and composition (%)  | Waste reprocessing/dumping  |
|------------------|---|--|---|
| 1                | Binani Zinc, Kerala (Thomas, 1998)  | Jarosite residue Zn: 3–5%, Fe: 20–28% Pb: 8–10%, SO <sub>4</sub> : 40–46% Primary cake leach residue Zn: 2–4%, Cd: 0.5–2%, Cu: 40–50%, Co: 0.02–0.03%  | Stored inside the premises in a large pond of 14,000 Mt (Seth, 1998) lined with LPDE sheets Both primary and secondary leach residue stored inside the premises in a covered shed provided with acid proof bricks at the bottom |
|                  |   | -Secondary leach residue<br>Zn: 20–30%, Cd: 1.5%, Cu:<br>10–15%, Co: 0.2–0.5%  | Dumped and commercial disposal  |
| 2                | HZL Chanderia, Rajasthan<br>(Mackenzie and Smith, 1981;<br>Sharma, 1989, 1998)  | ISF Slag 42,000 t per year<br>Zn: 6–9, Pb: 0.6–0.7, Cu: 0.19,<br>Sb: 0.01, Ag: 19 g/Mt, Au:<br>0.04 g/t, FeO: 33<br>-Effluent plant sludge (Details<br>of other wastes covered in lead<br>section) | Goes for Cadmium recovery.  |
| 3                | Debari Smelter plant, HZL,<br>Rajasthan (Bhatnagar and<br>Jancy, 1998; Basu and<br>Swarnkar, 1990; Jaju, 1998;<br>Sharma, 1989; Solanki and<br>Singh, 1981) | Drum Cake Zn: 17, Fe: 32, Pb: 5.4, S: 5.4, Cd: 0.25, Cu: 0.11, Co: 0.003, Ni: 0.005, MgO: 0.6, Mn: 2.1, Sb: 0.004, As: 0.05, CaO: 3.0, SiO <sub>2</sub> : 3.9, Ag: 0.038                           | Goes for Ag recovery  |
|                  | oligi, 1701)  | Cadmium cake Zn: 36, Cd: 14.0, Cu: 2.2,  | Goes for Cd recovery  |
|                  |   | Beta cake<br>Zn: 9.16, Cu: 0.05, Cd: 0.5, Mn:<br>2.6, Co: 1.45, Ni: 0.31, Fe: 3.33   | For Co recovery (mostly stored)   |
|                  |   | Jarosite residue: 41,000 t per<br>year<br>Zn: 3–4, Fe: 19–20, Pb: 3–4,<br>Cu: 0.04, Cd: 0.07, CaO: 12.0,<br>SiO <sub>2</sub> : 4.0, Al <sub>2</sub> O <sub>3</sub> : 4.4,                          | Dumping   |
|                  |   | -Zinc tailing Zn: 16.3, Fe: 29.5, Pb: 7.0, Cu: 0.31, Cd: 0.26, Ag: 0.013, MgO: 0.8, CaO: 6.4, SiO <sub>2</sub> : 5.3,  | Dumping   |
| 4                | Zinc Lead Smelter plant, HZL,<br>Visakhapatnam (Sharma, 1998;<br>Solanki and Singh, 1981;<br>Thomas, 1998)  | Al <sub>2</sub> O <sub>3</sub> : 5.9, S: 0.36<br>Moore cake  Pb: 5.6–5.8, Fe: 22–25, Zn: 20–22, Cd: 0.05–0.075, Ag: 0.0125, Ca: 3–4.   | Transferred to Waelz Kiln for zinc recovery as zinc oxide Goes to klinker klin for separation of zinc, cadmium and lead and leaching of zinc in main unit.  |

Table 6 (Continued)

| Serial<br>number | Name of the industry      | Waste generated: quantity and composition (%) | Waste reprocessing/dumping |
|------------------|---------------------------|---|----------------------------|
|                  |                           | Raw zinc oxide: 6950 t per year               | _                          |
|                  |                           | Zn: 55–60, Pb: 7–10, Ag:                      |                            |
|                  |                           | 60 ppm, Cu: 0.01–0.03, As:                    |                            |
|                  |                           | 0.03, Sb: 0.01–0.03, F:                       |                            |
|                  |                           | 0.05-0.09, C: 1-2, FeO: 1.0,                  |                            |
|                  |                           | Cd: 0.28, CaO: 0.2, MgO: 0.2,                 |                            |
|                  |                           | Al <sub>2</sub> O <sub>3</sub> : 0.8–1.0      |                            |
|                  |                           | Sintered zinc oxide: 6950 t per               |                            |
|                  |                           | year  |                            |
|                  |                           | Zn: 65, Pb: 8-9, Cd: 0.02                     |                            |
|                  |                           | Clinker product                               | _                          |
|                  |                           | Zn: 58–62, Pb: 5–7, SiO <sub>2</sub> : 5.0,   |                            |
|                  |                           | Fe: 3-5, Cd: 0.01-0.015, Ag:                  |                            |
|                  |                           | 0.0042  |                            |
|                  | Sunrise zinc, Cuncolim,   | Sludge 2400 t per year                        |                            |
| 5                | Goa (Bhatnagar and Jancy, | Zn: 1.26, Cu: 1.65, Fe: 2.94,                 | Waste is disposed off in a |
|                  | 1998)                     | Al: 0.6, Pb: 1.42, Si: 3.8,                   | secured land fill          |
|                  |                           | Gypsum: 24.5                                  |                            |
| 6                | Bharat zinc               | Filter cake                                   | Secured land fill          |

recycling of tailing dam water to beneficiation plants as process water so as to maintain zero discharge, green belt development to improve landscape, to work as dust sinks and achieve noise attenuation. At its open pit Rampura Agucha Mine, a number of measures have been taken to ensure minimum ground vibrations due to blasting, and each and every blast is monitored for the vibration levels.

At the smelting units, the environmental protection measures include sulphuric acid plants on double conversion double absorption (DCDA) technology to ensure minimum sulphur di-oxide emissions. Single conversion single absorption (SCSA) sulphuric acid plants also have been provided with Tail Gas Treatment facilities for ensuring minimum sulphur dioxide emissions. In addition, other elaborate dust collection and gas cleaning facilities have been provided to ensure minimized gaseous emissions. Integrated effluent treatment plants have been provided to ensure that treated effluents meet all the criteria stipulated by the Central Pollution Control Boards.

The waste generated as tailing in the concentrator plant at HZL though not included in this article is mostly dumped in the specific area, besides the back filling and in the tailing dams and also used in constructing embankment, mine road, play ground, filling low lying area etc. The major wastes generated from the smelters are the leach residues and the jarosite residues. The residue treatment plant at Debari, HZL is in operation to treat and recover zinc and other metal values. The final waste, jarosite cake is disposed off in storage pond after lime addition to render it inert. The intermediate residues like drum cake and cadmium containing cake are processed for the recovery of Ag and Cd in these units.  $\beta$ -cake is another material consisting of cobalt, and is mostly stored for Co recovery (Bhatnagar and Jancy, 1998). The process used for Co recovery involves fluidized bed roasting of  $\beta$ -cake followed by  $H_2SO_4$  leaching, solution purification, solvent extraction and electrowinning. The pilot

| Element          | Brass dross (%) | Brass ash (%) |            |
|------------------|-----------------|---------------|------------|
|                  |                 | Imported      | Indigenous |
| Zn               | 41–42           | 50–55         | 20–30      |
| Cu               | 43–45           | 12–15         | 4–5        |
| Fe               | 1–2             | 1–2           | 1.5-2.5    |
| Cd               | Nil             | Nil           | Nil        |
| Pb               | Nil             | Nil           | Nil        |
| Ni               | 0.02-0.5        | 0.03 - 0.06   | 0.05-0.07  |
| Cl               | 0.1-0.5         | 0.2-0.5       | 0.1-0.3    |
| SiO <sub>2</sub> | 1–2             | 2–3           | 5-20       |

Table 7
Composition of brass ash/dross used by some of the Indian Industry

plant installed at Debari (HZL), Udaipur for Co recovery is not utilized for continuous production of this metal. Maximum recovery of cobalt from  $\beta$ -cake is reported to be about 60%.

The imperial smelter furnace (ISF) slag generated at Chanderia unit is mostly stored in a separate dump yard with minor commercial disposal. Though the slag is vitreous in nature the toxic constituents are in sufficient amount and may prove to be hazardous due to mobility of the ions by weathering action.

Manufacturers of the secondary zinc use indigenously available secondaries and imported materials (Zn ash/dross/skimming, EAF dust). Two types of dross namely top dross that floats on the top of the bath and the bottom dross that sinks to the bottom of the galvanising bath based on the specific gravity of the material, are obtained. They account for 10–20% loss of Zn during galvanising. Zinc content in drosses lies in the range 90–96% (Table 7).

The most important source for input of secondary zinc is therefore the inevitable waste arising from the galvanising industry such as (i) zinc dross, (ii) zinc ash, (iii) flux skimmings and (iv) steam blowings from tube galvanising. The chemical composition of these wastes is incorporated in Table 8.

Quite often the technology followed is hydrometallurgical based involving leaching, metal purification, separation, precipitation and electrolysis. In some of the units, ZnO is manufactured from the secondary zinc following pyrometallurgical processes, which

| Table 8  |
|--|
| Normal range of constituents in galvanising residues |

| Element | Zinc dross (% | (6)    | Zinc ash (%) | Zinc skimmings (%)     |
|---------|---------------|--------|--------------|------------------------|
|         | Тор           | Bottom |              |                        |
| Zn      | 93–96         | 93–96  | 50–75        | 50–60                  |
| Pb      | 0-0.5         | 1–2    | 0.2-2.5      | 0-1.5                  |
| Al      | 0.5-4         | 0-1    | 0-0.3        | 0-0.5                  |
| Cd      | _             | 0-0.2  | 0.05 - 0.1   | 0-0.2                  |
| Fe      | 0.5-3         | 3–6    | 0.2-1.5      | 0-1                    |
| Cl      | _             | _      | 1-6.5        | 10–25                  |
| Others  | _             | _      | _            | NH <sub>4</sub> Cl 3.1 |

involves carbon reduction and vaporisation of zinc followed by controlled oxidation to produce ZnO. Waste is mostly in the form of residues, which are often disposed off as unsystematic landfills, though some industries follow the safe handling and disposal procedure laid down officially by monitoring agencies.

Over the years zinc sulphate industry dealing with micronutrients has developed technology for handling air, water and solid wastes (Agrawal, 1998). The sludge obtained in the process from the filter press is washed to recover both water soluble and acid soluble zinc and washing is then recycled. This sludge is given a treatment of excess lime, which converts water-soluble zinc to insoluble form. Lead that is present originally in the zinc ash (0.3–0.8%) will also report in the sludge as insoluble form of lead metal/oxide or lead sulphate. To ensure that treated sludge does not carry any soluble salts of heavy metal ions, it is kept for 10–15 days for curing before final disposal. The treated sludge is disposed off which may cause some damage to the environment in the long run unless environmental impact analysis (EIA) finds it otherwise.

### 5. Lead industries

There are two major organisations namely Hindustan Zinc Ltd. (HZL) and Indian Lead Ltd. (ILL) producing lead metal in India. The production capacity of HZL is 65,000 Mt and that of Indian Lead Limited is 24,000 t per year lead. The ILLuses scrap battery as well as lead concentrates. There is also a secondary lead production capacity of 15,000–20,000 t per year in the unorganised sector numbering as high as 2500 in various parts of the country. About 60% of lead production is from secondary sources world over.

Currently over 70% of the lead consumed by automobile industry India is fed by the secondary lead smelting plants (Pugazhenthy, 1998), mainly derived from the used acid batteries. Spent battery falls under the category of restricted materials and hence must be handled with utmost care owing to the toxic effects of lead and dangers of sulphuric acid. Non-separation of the scrap batteries/compounds and smelting the whole battery with its plastic body produces poisonous dioxine, which is detrimental and hazardous to the public health causing damage to the environment.

Obviously, lead-acid battery is the dominant source of secondary lead yet the metal also comes from a variety of sources such as damaged/old scrap, obsolete or worn-out products including bearing metals, sheets and pipes, cable sheathing and solder as well as dust and drosses. The primary lead industries in smelting and refining are equipped with pollution control facilities to take care of air and water pollution. The small-scale secondary refineries mostly in the unorganised sectors are causing maximum pollution affecting human being and environment. This is mainly due to improper technology, cash crunch and lack of monitoring and implementation of pollution norms. Similarly the solid waste management attracts some attention in primary lead unit, but the same is not given much importance in secondary industries.

#### 5.1. Waste treatment/disposal practices in lead industries

The details of waste generated, their quantity, composition and disposal practices of some of the major lead plants are incorporated in Tables 9 and 10. Dumping or stockpiling of lead

Table 9
Details of metallic waste in primary lead industry

| Serial<br>number | Name of the industry   | Waste generated: quantity and composition (%)   | Waste: reprocessing/dumping  |
|------------------|--|---|--|
| 1                | Zinc lead smelter, HZL,<br>Visakhapatnam<br>(Jagannathan, 1981)<br>(presently shut down) | BF slag: 15,000 t per year Pb: 1.5–2.0, SiO <sub>2</sub> : 20–22, FeO: 36–38, MnO <sub>2</sub> : 3.0, CaO: 14, MgO: 2.0, Al <sub>2</sub> O <sub>3</sub> : 6–7, Zn: 5–7, S: 2.0 Ordinary Cu dross Pb: 83.0, Ag: 0.09, Cu: 2.0, Zn: 1.0, Sb: 0.3, Bi: traces Antimony dross Pb: 70.0, Ag: 0.05, Cu: 0.3, Zn: 1.0, Sb: 2.0, Bi: traces Final refinery dross Pb: 72.0, Ag: 0.03, Cu: 0.2, Zn: 5.2, Sb: 0.5 Enriched liquated silver crust Pb: 78.0, Ag: 5.8, Cu: 0.7, Zn: 14.0, Sb: 0.1 | Part of the slag is recycled and rest is dumped  |
| 2                | Tundoo lead smelter,<br>HZL, Bihar (Mukherjee,<br>1981)                                  | BF slag: 18, 000 t per year<br>Pb: 1.5–2, FeO: 32–35, ZnO: 9–12,<br>MgO: 4–4.5, insoluble: 23–24, CaO:<br>14–16, Al <sub>2</sub> O <sub>3</sub> : 9–10, Ag: 0.001–0.002<br>Copper and ordinary drosses: 300 t per   | Part of it is recycled in the sintered section. Rest is dumped  For silver lead recovery |
|                  |  | year Cu: 2–4.5, Pb: 80, As: 10–11 Prest crust: 375 t per year Ag: 4–5, Zn 15–18, rest: Pb Dezincing and antimony drosses: 1.5 t per year  | Goes for Ag recovery   |
| 3                | HZL Chanderia,<br>Rajasthan (Mackenzie<br>and Smith, 1981; Sharma,<br>1989)              | Litharge: 480 t per year ISP slag 42,000 t per year Zn: 6–9, Pb: 0.6–0.7, Cu: 0.19, Sb: 0.01, Ag: 19 g/t, Au: 0.04 g/t, FeO: 33 Matte & Speiss: 1300 t per year Pb: 17.3,Cu: 44.6, Sb: 1.2, Ag: 19.50 g/Mt, Au: 1.9 g/t   | Dumped and commercial<br>disposal  Commercial disposal for Cu<br>recovery or stored      |
|                  |  | Antimony drosses 1520 t per year<br>Pb: 51.5, Cu: 0.9, Sb: 7.0<br>Silver crust (enriched): 370 t per year,<br>Pb: 24, Cu: 2.4, Ag: 15 g/t, Au: 0.012  | Stored or sold to battery makers  Reprocessed for Ag recovery                            |
| 4                | Indian Lead Ltd., Thane<br>(Thadani, 1996)   | Ferrosilicate slag: 3000 t per year<br>FeO: 40–50, CaO: 10–20, SiO <sub>2</sub> :<br>35–45, Pb: <2.0  | Slag containing lead >2% is recycled and discarded only when lead content is <2%.        |

blast furnace slag, ISF slag and flue dust is mostly followed in primary lead units. Though the slags are vitreous in nature this mode of disposal is now questionable on environmental and economical grounds. The by-products of these units like enriched silver crust/prest crust and copper dross in HZL plants are mostly processed for the recovery of silver and

Table 10
Details of metallic waste in secondary lead industries

| Serial<br>number | Name of the industry                                      | Waste generated: quantity and composition (%)  | Waste: reprocessing/dumping  |
|------------------|---|--|--|
| 1                | AMCO Batteries Ltd.,<br>Bangalore (Mallikarjuna,<br>1998) | Lead process scrap: 4000 t per year  | Process waste is sent for reclamation  |
|                  | ,   | ETP sludge: 4t per year  | Sludge is stored in an impervious tank in their own land.                                    |
|                  |   | Mixture of Pb, PbO, PbO <sub>2</sub> , PbSO <sub>4</sub> ,   |  |
| 2                | Shirin Metals Ltd., Valsad,<br>Gujrat (Kuraishi, 1999)    | Slag: 24 t per year<br>Pb: 1-2.5, CaO: 10-15, Fe <sub>2</sub> O <sub>3</sub> : 15-20,<br>Na <sub>2</sub> O: 4-5, SO <sub>4</sub> : 10-15 | Slag is disposed off to the sited<br>demarked by GIDC after<br>washing with sprinkled water. |
|                  | Amara Raja, Tirupati<br>(Naidu et al., 1999)              | Solid waste: 297 t per year  | Sold to indigenous authorised smelters   |
|                  |   | Mixture of Pb, PbO, PbO <sub>2</sub> , PbSO <sub>4</sub>   |  |

lead metals. Matte and speiss generated are stored or sold for copper recovery. Antimony dross of HZL Chanderia is stored or sold to battery makers. The ferrosilicate slag containing >2% lead generated in Indian Lead Limited is recycled to extract lead and discarded only after lead content is brought down to <2%. Presently the slag is stored inside the factory premises for want of suitable land site allocation by the respective State Pollution Control Board (SPCB).

Industries in the organised sector like Hindustan Zinc Ltd. and Indian Lead Ltd. follow the proper process and to some extent waste management technology. Since lead is a very toxic material, disposal of the solid wastes in the secured landfill is absolutely necessary. However, major problem is with the secondary lead smelting units and most of them do not follow the proper processing technologies and are handling the spent lead-acid battery scraps without resorting to the pollution control norms with respect to the SPM level, SO2, CO and lead fumes. A standard lead-acid battery generally has 70–80% lead metal and metal oxide, 5–6% polypropylene, 12% electrolyte (free H<sub>2</sub>SO<sub>4</sub>) and 2–3% others (Ebonite, PVC, Paper). During the processing of spent lead-acid battery in backyard units, operations like breaking, crushing, screening, dry mixing etc. generate airborne lead dust which directly or indirectly enter into the human system and the surroundings of the working area. Lead absorption into the human body in significant quantity causes lead poisoning. Several of these backyard smelters simply recover 60–70% of the metal using home made technologies because of the low melting point of the metal and simply throw the slag containing very high lead into the environment causing greater damage to nearby locality. The worst sufferers in the unorganised backyard smelters are the workers involved in these units and the environment affecting the local population.

It is of paramount importance to arrest the pilferage of lead battery scraps to these backyard smelters through legislation and proper monitoring and ensure collection of the spent batteries by the organised sector. The rotary kiln furnace process used by some of the secondary lead manufacturers in the unorganised sector needs to be modified particularly

| Country   | Lead in work<br>area (mg/NCM) | Lead in blood<br>(mg/100 ml)       | Lead in emissions (mg/NCM) | Lead in effluents (mg/l) | Lead in atmosphere (mg/NCM) |
|-----------|-------------------------------|------------------------------------|----------------------------|--------------------------|-----------------------------|
| Australia | 0.15                          | 70 <sup>a</sup><br>30 <sup>b</sup> | 10                         | 0.05                     | 1.5                         |
| Austria   | $0.10^{a} \ 0.02^{b}$         | 100 <sup>a</sup>                   | 10                         | 0.05                     | -                           |
| Canada    | 0.15                          | 70                                 | 29                         | 15                       | _                           |
| Denmark   | 0.10                          | 50                                 | c                          | 0.1 - 0.5                | 2.0                         |
| EEC       | 0.15                          | 70                                 | _                          | _                        | 2.0                         |
| Germany   | 0.10                          | 70 <sup>a</sup><br>30 <sup>b</sup> | 5                          | 0.2                      | 2.0                         |
| India     | 0.15                          | 80                                 | 10                         | 0.1                      | 1.5                         |
| UK        | 0.15                          | 70 <sup>a</sup><br>40 <sup>b</sup> | 10                         | Variable                 | 2.0                         |
| USA       | 0.1                           | 50                                 | Variable                   | Variable                 | 1.5                         |

Table 11 Emission control standards for lead plants (Thadani, 1996)

to handle the dust and smoke (gases) from the system, besides lowering lead level to less than 2% for proper disposal.

Regarding the pollution and its limits applicable to lead based industries the pollution control authorities are well aware of the nagging problems. The pollution control rules in India are similar to those in the developed countries. For example, the norms of emission from the stack as well as in the ambient air (Thadani, 1996) are as stringent as in the developed countries (Table 11). The organised smelters come under the scrutiny of law enforcing agencies and hence follow the norms and often take corrective measures to meet the regulations. A range of restrictions on the collection, handling, transport and processing of spent batteries, require monitoring of their movement both domestically and internationally.

Efforts need to be made to improve health protection of the workers and to reduce the quantity of lead entering to the environment, which can be met through:

- efficient collection of the acid battery scrap,
- strict control over unorganised sectors,
- modified working practice and adoption of eco-friendly process technologies.

# 6. Permissible limits of the metallic hazardous constituents

Extraction procedure for toxicity assessment is designed to identify wastes that are likely to attain hazardous concentrations of the particular toxic constituents into ground water as a result of improper management such as dumping. In this procedure the wastes are leached in a manner to simulate the leaching action that occurs in the landfills. The extract is analysed

<sup>&</sup>lt;sup>a</sup> Men.

<sup>&</sup>lt;sup>b</sup> Women.

<sup>&</sup>lt;sup>c</sup> Limit set for individual plants.

| Contaminants determined in TCL1 test |              |                            |                              |  |
|--------------------------------------|--------------|----------------------------|------------------------------|--|
| Serial number                        | Contaminants | EPA fazardous waste number | Maximum concentration (mg/l) |  |
| 1                                    | Arsenic      | D004                       | 5.0                          |  |
| 2                                    | Barium       | D005                       | 100.0                        |  |
| 3                                    | Cadmium      | D006                       | 1.0                          |  |
| 4                                    | Chromium     | D007                       | 5.0                          |  |
| 5                                    | Lead         | D008                       | 5.0                          |  |
| 6                                    | Mercury      | D009                       | 0.2                          |  |
| 7                                    | Selenium     | D010                       | 1.0                          |  |
| 8                                    | Silver       | D011                       | 5.0                          |  |

Table 12 Contaminants determined in TCLP test

to determine if it possesses certain toxic contaminants. If the concentration exceeds the regulatory levels then the waste is classified as hazardous.

Some of the regulatory levels (Manhan, 1994) of the contaminants in the leached extract are given in Table 12 as per guidelines of Environment protection Agency (EPA), USA which is accepted in India as well. It is therefore essential to test all the solid wastes from nonferrous metal industries in general and copper, zinc and lead primary and secondary units in particular, that are dumped without following proper procedure or used for landfilling.

The lack of informations in open literature on TCLP test results, clearly demonstrated the level of negligence prevailing in these industries on solid metallic waste management. The solid wastes produced from the liquid effluents are no longer the safer options unless these wastes are handled and managed/processed in eco-friendly manners adopting specified procedures laid down by the pollution enforcement agencies. NML, Jamshedpur is presently involved in the characterisation of solid wastes that are generated in Indian nonferrous metal industries to assess the environmental degradation.

## 7. Activity at National Metallurgical Laboratory

In the continuous effort for the development of processes and recovery of values from wastes and by-products of ferrous and non-ferrous industries some attempts have been taken during the past decades for the recovery metals and production of value added products from various wastes. A few of them are briefly enumerated.

Process was developed for the recovery of vanadium pentoxide/ferro-vanadium from sludges of alumina plants, utilization of fly ash for manufacture of bricks, tiles, etc. and recovery of metal values from red mud. Recently the possibility of making sinters suitable for iron blast furnace by using iron ore fines and red mud sand in various proportions have been explored with aluminium content varying from 3–4% and basicity of the sinter was in the range of 1.9–2.4 with no alkali and TiO<sub>2</sub> in the sinter sample. Converter slag from one of the Indian copper plant was characterized with respect to its hazardous/non-hazardous nature for its safe disposal/storage and was reduced and smelted to produce an alloy phase comprising of iron for application such as cast product/grinding media. Both pyro- and hydro-metallurgical processes have been developed for recovery of nickel as ferronickel/

Table 13
The tentative limits fixed for toxic elements in zinc ash for imports

| Serial number | Components | Percentage      |
|---------------|------------|-----------------|
| 1             | Zn         | 60 (minimum)    |
| 2             | Cu         | 1.7 (maximum)   |
| 3             | As         | 0.1 (maximum)   |
| 4             | Cd         | 0.1 (maximum)   |
| 5             | Cr         | 0.01 (maximum)  |
| 6             | Pb         | 1.25 (maximum)  |
| 7             | Ba         | 0.005 (maximum) |
| 8             | Hg         | 0.002 (maximum) |
| 9             | Se         | 0.004 (maximum) |

Work done at NML for MoEF.

nickel salt from various spent nickel catalyst. A process was developed for the production of electrolytic copper powder from copper waste solutions from one of the industries namely M/S Grishma industries and know-how was transferred to the industry after a successful run at our end. Attempts have also been made to recover zinc metal/compounds from secondary/waste materials. Zinc reclamation from zinc dross/ash/skimmings from galvanizing shops have been done at NML by various hydro-/pyrometallurgical processes. A data base on waste generation, its composition and recycling/disposal practice in the non-ferrous and ferrous industries have been prepared and recommendation for future R&D work for recovery and utilization of such wastes have been made. NML is involved in the chemical and toxicological characterization of solid wastes/secondaries for import and their safe disposal by various industries. In order to fix the limits of toxic elements in Zinc ash/skimming an effort was made at NML, based on the data available for head analysis and TCLP tests and the data based on the analysis of eleven samples gives tentative threshold limits (Table 13) of metal components in zinc ash/skimmings for import/export purposes. Final recommendation on these limits can be authenticated only when TCLP test on a large number of samples from different processes and origin is carried out. This could facilitate the import of zinc-based secondaries for the time being without resorting to TCLP test. In the intervening period ministry of Environment and Forest has accepted the limits of the toxic radicals suggest above for selective imports of zinc secondaries and permitted imports to a number of recycling units possessing necessary processing technology and waste handling and disposal expertise/facilities, in the overall interest of the nation. A permanent solution to this problem is yet to be found out unless complete test results mentioned above are available.

## 8. Conclusion

Most of the pollution control technologies adopted today convert the pollutant from one
form to other like in effluent treatment plant aqueous pollutant may be converted into
solid waste which is discharged either in open or secured landfill. Both are undesirable
from the land point of view, which need to be preserved for future generation.

- 2. A lot of efforts have been put in to find useful application of the red mud and fly ash, but the tangible products with proper economic implications are yet to be fully realised. Presently some small fractions of these wastes are used as building material and road making. Similarly recycling of SPL for reduction purposes as a supplement to coke/flux in electric arc furnace iron making may be established. Till then proper treatment and storage of SPL are the only option to the aluminium industries to avoid fluoride mobility.
- 3. A number of solid wastes generated in the copper smelters are treated by pyro/hydro-metallurgical methods/recycled to recover valuable metals while leaving minimum amounts of wastes for disposal. These are converter slag, dust, anode slag, anode slime, ETP sludge, etc. The granulated slag/slag after copper flotation are dumped near the smelters. However, the hazardous constituents in these slags particularly Se, Te, Hg, Ag, As, Pb and Cu may enter in the water stream due to the weathering action and rain water.
- 4. Most of the zinc producing industries in primary sector are having more or less acceptable waste management control facilities. However, besides only a few, most of the secondary processing units have no such facilities causing maximum pollution. Because these units use imported zinc ash, skimmings, drosses contaminated in plenty with several toxic elements also, the wastes/residues generated from their processing are expected to create environmental degradation on dumping.
- 5. In order to control the pollution caused by the unorganised lead sector, a legislation as well as appropriate monitoring are to be evolved and enforced for a systematic collection and its recycling in the units having eco-friendly and waste management process technologies. The slags produced from the primary and secondary lead processing industries must be disposed off to the sites as per specification/instructions laid down by the Pollution Control Boards.
- 6. The existing wastes generated and accumulated from various non-ferrous process industries over a long period should be characterized (TCLP and water extract) for its hazardous or non-hazardous nature and a procedure has to be evolved in consultation with industry and CPCB/SPCB/different laboratories for its safe disposal.
- 7. In addition to increased utilisation of solid wastes, efforts are needed towards waste minimisation by attacking the problem at its source, which not only maximise production and product quality, but also minimise the overall environmental impact by: technology upgradation/use of eco-friendly technology, improvement in the quality of raw material, audit on waste minimisation, adopting innovative management strategies, conducting employee awareness programme.

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