

## **RECYCLING OF METALS FROM SECONDARY SOURCES TREATMENT OPTIONS**

**K. K. SAHU AND A. AGRAWAL**

Email : [kksahu@nmlindia.org](mailto:kksahu@nmlindia.org), [archana@nmlindia.org](mailto:archana@nmlindia.org)

### **INTRODUCTION**

Metallurgical industries generate vast quantities of solid wastes such as slag, ash, sludge, dross, grindings, turnings, clippings, residues and secondaries. During the last two decades rapid industrialization has led to many fold declines in the quality of environment. Some of the solid wastes produced during the metal extraction are hazardous in nature, since they contaminate the surface and ground water through the leachate generated at the dump-sites putting the life of the living organism at a risk. But, the effects of pollution due to the toxic constituents of the above leachate, are usually noticed in 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. Therefore, there is a need of concerted efforts involving more research and development work in tandem with the production units so as to achieve the implementation of the cleaner technologies for metal production, waste processing, handling and recycling. In this paper, the kind of solid wastes generated by the Indian lead, zinc, copper and aluminium industries, their treatment and disposal procedures are discussed in a comprehensive manner.

### **LEAD**

#### **Lead Industries in India**

India has two major primary lead producers namely Hindustan Zinc Ltd (HZL) and Indian Lead Limited (ILL) with annual production capacity of 65,000 and 24,000 tonnes respectively. India's largest refinery being setup by Sterlite-managed by Hindustan zinc group with an annual capacity of 50,000 tonnes inside the premises of HZL's Chanderia Lead Zinc smelter with the help of Australia based Ausmelt technology. There are about seven medium size secondary lead plants (total capacity 55,000 tonnes/year), 40 small operations (combined capacity of 15,000 tonnes/year) and more than 250 tiny/backyard plants (estimated combined capacity 25,000 tonnes/year). The main source of lead in these plants is scrap batteries. The overall contribution of the secondary lead industry in the country is almost same as that of primary producers. Around 52,000 tons of secondary lead is produced from the organised sectors but only 30,000 tons are available in the open market as the remaining part goes to captive consumption. Lead production from unorganised sectors (backyard smelters) is about 15,000 tons per year. The demand of lead, which cannot be met by primary production, can be compensated to some extent by secondary production.

## Secondary Lead Processing

The chief source of old scrap is lead-acid batteries and other sources include cable coverings, pipe, sheet, and other lead-bearing metals. Over 70% of the world's total output of lead is consumed in the manufacture of lead-acid storage batteries. At the end of their life, such batteries are readily collected and become the major feed to the secondary lead industries.

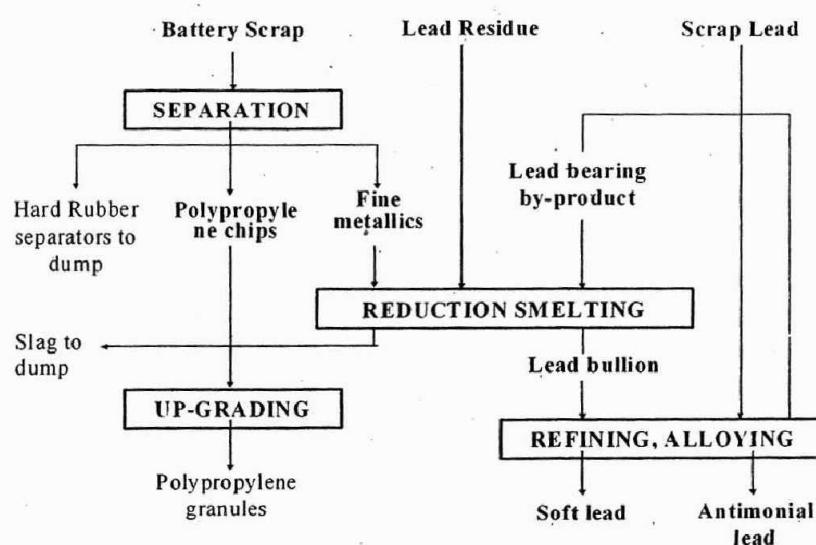
Almost all the secondary plants use the pyro-metallurgical smelting process. Battery scrap from automobile sector accounts for 80% of old scrap recycled as secondary lead raw material. A standard lead acid battery for starting, lighting, and ignition of vehicles has the following average composition by weight:

Lead metal	:	34%	Electrolyte (free sulphuric acid)	:	11-12%
Lead oxide paste	:	39%	Others (ebonite, PVC, paper etc)	:	8 -10%
Polypropylene	:	5 - 6%			

Prior to smelting, batteries are usually broken up and sorted into their constituent products. Fractions of cleaned plastic (such as polypropylene) case are recycled into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal or recycled to the local acid market. One of the three main smelting processes (blast furnaces, rotary furnaces, or reverberatory furnaces) is then used to reduce the lead fractions and produce lead bullion.

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and generation of waste sludge during smelting (Fig-1). Battery paste containing lead sulfate and lead oxide is desulfurized with soda ash, yielding market-grade sodium sulfate as a byproduct. The desulfurized paste is processed in a reverberatory furnace, and the lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

Spent battery scraps are the source of 80% lead that is recycled in India. It may be noted here that most of the lead recyclers are small-scale enterprises where lead recovery potential is



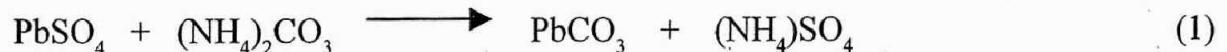
**Fig. 1 :** General flow-sheet for recovery of lead from spent batteries and other secondaries

less. Due to the nature of technology used by them, the pollution potential is much higher than the recovery aspect. They use an open kiln or a pot called bhatties for smelting. Used batteries auctioned through disposal programmes of large scale users like the railways often go to traders/backyard (cottage) type of industries who cannot afford suitable facilities for recycling. Being small units they escape the legal net. As a result, recycling of hazardous lead takes place openly and without safeguards, thus causing much harm to the environment rather than contributing positively to the national economy. Therefore, suitable legal action in this context is necessary to effectively handle of hazardous lead wastes by such units.

### Newer Hydrometallurgical Processes

With the prospect of even tighter environmental controls, several efficient and eco-friendly hydrometallurgical processes have been developed to treat lead acid battery scrap particularly the battery paste/sludge. Most of these processes are either on laboratory scale or tested on pilot scale of operation and probably not yet economic in comparison with the pyrometallurgical processes. The object of the processes in most cases is to fix the sulphur as a harmless sulphate and to put the lead into a suitable solution for electrolytic recovery. Few processes suitable for processing battery scrap are described below.

**RSR Process :** In this process the  $\text{PbSO}_4$  portion of the battery sludge is treated with ammonium/alkali carbonate to produce lead carbonate and ammonium sulphate.



Insoluble  $\text{PbO}_2$  part of the sludge can be reduced to soluble form by the addition of  $\text{SO}_2$  to an alkali/ammonium carbonate producing alkali sulphite/bisulphite which reacts with  $\text{PbO}_2$  to produce  $\text{PbSO}_4$ . Sulphite/bisulphite is oxidised to sulphates and lead is precipitated as  $\text{PbCO}_3$  or  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ .

**Bureau of Mines Process :** Like RSR process the sludge (containing  $\text{PbSO}_4$  and  $\text{PbO}_2$ ) is pre-treated with ammonium carbonate to desulphurise  $\text{PbSO}_4$ . Here the reduction of  $\text{PbO}_2$  to  $\text{PbO}$  is done by addition of metallic lead powder during leaching with  $\text{H}_2\text{SiF}_6$ . The drawback of this process is the requirement/recycling of large amount of powder lead, as the  $\text{PbO}_2$  content in the sludge is about 35-40%. This process utilises  $\text{PbO}_2$  coated titanium anodes and lead cathodes and about 1-2 g/L of phosphorous to prevent  $\text{PbO}_2$  deposition on the cathode. The lead content in the electrolyte may be as high as 150 g/L and depleted lead level is above 25-35 g/L.

**Engitech Process :** The process is suitable for paste and sludge in which the desulphurised sludge containing  $\text{Pb}$ ,  $\text{PbCO}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ , and  $\text{Pb}(\text{OH})_2$  is leached with  $\text{HBF}_4$  (Eq 2). The process also uses  $\text{H}_2\text{O}_2$  to dissolve  $\text{PbO}_2$  (Eq. 3).

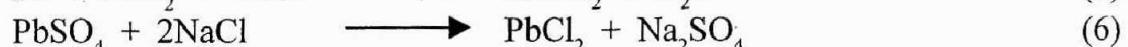
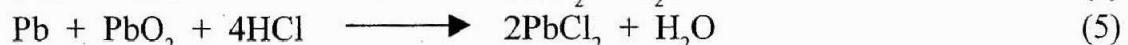


To avoid  $\text{PbO}_2$  deposition at anode, the Engitech process utilises a specially designed composite anode, that operates at high anode current density ( $320 \text{ A/m}^2$ ).

**Ginata Process :** In this process lead acid batteries are activated electrolytically in dilute  $H_2SO_4$  to convert  $PbSO_4$  to  $H_2SO_4$ . After activation the plates are short circuited in fluoboric acid electrolyte where lead is oxidized and dioxide is reduced with the formation of highly soluble fluoborate. The resultant fluoborate electrolyte is electrowon in presence of about 200 ppm cobalt as additive eliminating the need for  $PbO_2$  coated or special alloy anode. Cobalt enhances the evolution of oxygen and thus minimises the degradation of graphite anode.

**AAS Process :** This process utilises ammoniacal ammonium sulphate (AAS) solution for the leaching of the battery scrap. The crushed batteries are fed to an upward moving leaching column, where the solution floats the cases and separators(ebonite) out of the column, suspend and dissolve the lead compounds of the paste separating the clean metallic lead fraction. The  $PbO$  and  $PbSO_4$  dissolve in AAS solution and undissolved  $PbO_2$  is separated and converted to  $PbSO_4$  using about 50%  $H_2SO_4$  at high temperature. The resulting  $PbSO_4$  is fed back to the AAS leaching process. The lead is electrowon to get sponge lead. This process utilises ammonia and water as feed and recovers  $(NH_4)_2SO_4$  as by-product through a bleed stream.

**PLACID Process :** This process involves direct chloride leaching rather than disulphurisation and leaching with  $HBF_4$  or  $H_2SiF_6$ . The chemical equations of chloride leaching of battery paste are :



The soluble impurities are precipitated with lead powder as



The  $PbCl_2$  is dissolved in HCl and fed into the cathode compartment of a diaphragm cell for lead electrowining. Though the PLACID process and other chloride processes are attractive from environmental point of view but have not found favour because lead is recovered as a sponge and large amount of lead powder is required to reduce  $PbO_2$ .

From the environmental point of view, lead recovery from battery sludge via hydrometallurgical and electrowinning process looks attractive. But none of the above described processes have become operational.

## ZINC

### Zinc Industries in India

The three out of the four plants installed in India are operating on hydrometallurgical process route, whereas the fourth one at Chittaurgarh, Rajasthan, which was commissioned in the year 1991 is based on imperial smelting process route for simultaneous extraction of lead and zinc.

Earlier the installed smelting capacity for zinc in India was 199,000 MT of which HZL had 169,000 tonnes (Debari : 59,000 MT, Visakhapatnam : 40,000 MT, and Chanderia : 70,000 MT). After being taken over by Sterlite group HZL has raised its production capacity to

220,000MT a year by improving efficiency. Recently HZL has further expanded the capacity to 400,000 tonnes. Binani Zinc Ltd .(BZL) is estimated to produce 35,000 MT in 2004-05. The demand for refined zinc is 400,000 tonnes in the fiscal year of 2004-05 which is growing at a rate of 12-15% annually. HZL uses mainly indigenous zinc concentrate and occasionally imports from other countries while Binani Ltd. uses imported concentrates only. About 15-20% of zinc demand in India is met through secondary production against world average of 32-35%. There are about 40 secondary zinc units in India having a capacity of about 60,000 MT but actually producing 30,000 - 35,000 MT play a balance role in bridging the demand-supply gap.

### **Secondary Zinc Processing**

All zinc wastes containing zinc have been categorized as hazardous waste under the Basel convention. Some selected dross, zinc scrap and skimming are in green list of waste and zinc ash happens to be in amber list. Recycling of zinc offers both environmental and economic benefits by: (i) reducing energy required for mining and processing (ii) reducing volume of material that end up on land filling (iii) relieving environmental impacts on the land and water and (iv) conserving zinc ores.

The important sources of secondary zinc available for recycling are: pure zinc scrap in the form of sheet cuttings, zinc roofing, old zinc anodes etc., alloys containing zinc as a major constituent such as die casting alloys, brass dross/ash and scrap, other scrap alloys, zinc rich residues like zinc dross, zinc ash/skimmings and blowings from galvanising industries. The normal range of constituent in galvanising residues and other zinc sources are given in Table-1.

**Table 1 :** Normal range of constituents in Galvanising residues

Element	Zinc Dross (%)		Zinc Ash (%)	Zinc skimmings (%)
	Top	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	-	-	-	NH4Cl - 3.1

World over the contribution from different sources of zinc for recycling include the following, which are processed world wide through both pyro- as well as hydrometallurgical methods.

Brass scrap	:	32%	Zinc sheet	:	10%
Die casting scrap	:	16%	Steel plant dust	:	8%
Galvanising residue	:	23%	Others	:	11%

### **Pyrometallurgical Processing of Zinc Secondaries**

There are various pyro-metallurgical processes depending on the zinc concentration in the secondary feed, such as Electrothermic process for high and low zinc contained residues and Imperial Smelting Furnace (ISF) process for medium zinc contained.

Waelz kiln or QSL process, Larvic process, New Jersey's continuous vertical retort zinc distillation process, SKF plasma process, Mintek Enviroplas are used world wide. Waelz kiln process is most extensively applied in the pyrometallurgical treatment of residues. About 76% of total electric arc furnace (EAF) dust is treated by Waelz kiln in USA, Japan and Europe.

**AUSMELT Process :** Zinc is recovered from electric arc furnace (EAF) dust by bath smelting technology. Here oxygen, flux and coal are injected via a cooled lance into liquid slag in one furnace to melt the EAF dust and in the second furnace to reduce the zinc, lead and cadmium oxides. The fumed zinc, lead and cadmium are reoxidised above the bath and collected in a bag filter. Non-hazardous iron rich slag is prepared for disposal.

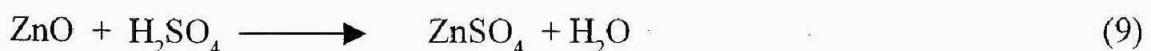
**WAELZ KILN Process :** In the two stage Waelz kiln process the raw dust is fed to the first kiln, to separate Zn, Pb, Cd and chloride from the non-hazardous partially metallized iron. The dust from the first kiln is retreated in the second kiln to produce impure ZnO for Zn smelter feed and lead-cadmium chloride for processing to separate lead and cadmium.

The single stage Waelz kiln process is identical to the first stage of the two stage process. The ZnO is generally treated in the Imperial Smelting Process to produce zinc and lead metal or converted to zinc-based chemicals and fertilizer additives.

### **Hydrometallurgical processing of zinc secondaries**

In India, the use of pyrometallurgical techniques for the recycling of zinc waste has been of less significant and mostly hydrometallurgical processes are practiced. Hydrometallurgical methods are comparatively cleaner and can be adopted in small and medium scale industries. The three main hydrometallurgical methods for treating the secondaries such as zinc ash/ skimming, brass ashes etc. are :

**Electrowinning Process :** The process generally uses zinc ash and other raw materials containing low level of impurities such as copper, cadmium etc. The processing steps mainly consist of material preparation, leaching, purification, electrowinning and melting. The material is crushed and pulverised to separate metallic zinc from fine ash. GOB (Good Ordinary Brand, 98.5% pure) zinc is obtained on melting and casting the separated metallic zinc. Fine ash is subjected to calcination to remove chlorides and is treated with sulphuric acid/spent electrolyte to get zinc sulphate solution as per Eq. 9.



The dissolved iron is oxidized and precipitated along with other minor impurities such as Al and partially As, Sb, etc. The solid filter cake generated is sent for disposal after suitable treatment and the filtrate containing concentrated zinc sulphate along with minor impurities like Cu, Cd, Co, Ni, As, Sb, Ge etc. undergo series of purification mainly with zinc powder and charcoal. The purified solution is cooled and electrowon using lead anodes and aluminium cathodes. Acid generated during electrolysis is utilised for further leaching.

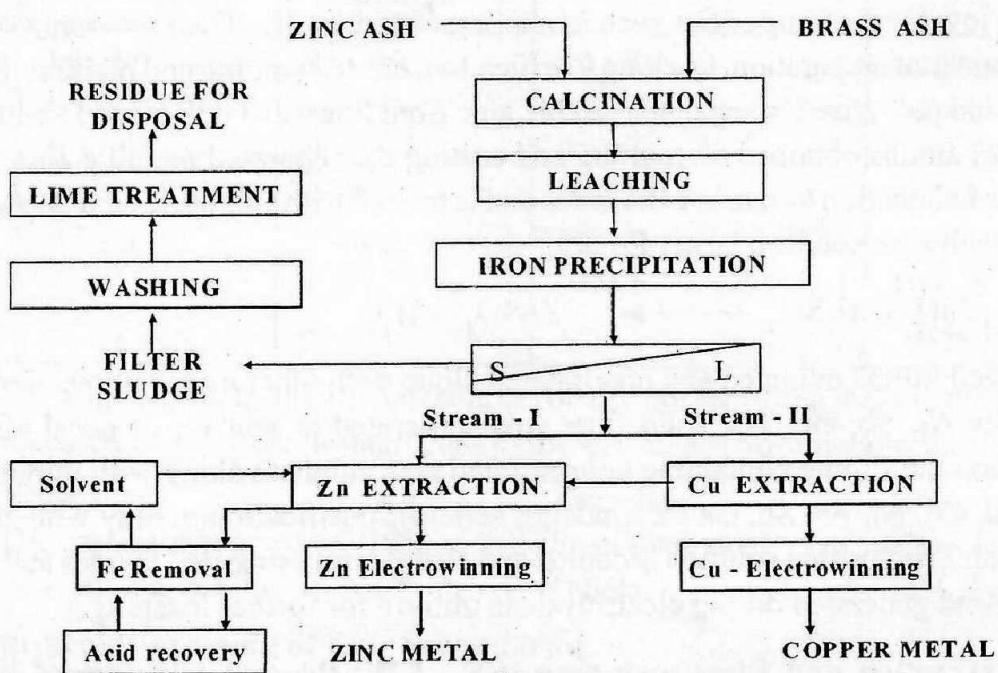
**Solvent Extraction and Electrowinning (SX - EW) Process :** In case of high copper containing material particularly brass ash, removal of copper by zinc dust cementation method is not attractive. Therefore copper is removed by solvent extraction to produce copper metal

as shown in Fig. 2. The solvent extraction process is carried out in a series of mixer-settlers which consist of three sub sections, namely (i) extraction, (ii) scrubbing and (iii) stripping.

After leaching and iron removal the clarified filtrate containing zinc and copper, comes in counter current contact with a suitable solvent in the extraction stage. Zinc is extracted selectively by the organic phase along with traces of copper. The loaded organic after scrubbing is brought into counter current contact with spent electrolyte in the stripping section. The resulting zinc electrolyte goes to cell house for zinc electro-winning. Similarly for copper circuit, a parallel stream of clarified feed is taken for extraction with the help of another organic, which selectively picks up only copper and the depleted aqueous phase is sent back to leaching as raffinate. Stripping of copper from loaded organic phase and electrowinning are more or less same as that of zinc.

**Crystallisation process :** Zinc ash fines are separated from metallic granules in pulverisers fitted with cyclone separator and bag filters and then processed for zinc sulphate manufacture. The fine ash containing mostly zinc oxide is treated with sulphuric acid to bring zinc values to sulphate form and filtered to get clear zinc sulphate solution. The solution is evaporated in a crystalliser and crystallised by cooling through chilled water to recover zinc as zinc sulphate.

**ZINCEX Process :** This hydrometallurgical process resembles conventional zinc electro winning and is readily integrated with such a plant. EAF dust is leached with sulphuric acid to solubilize zinc and cadmium oxide and halides. The impure zinc sulphate solution is treated by solvent extraction to remove zinc and cadmium and transfer them to purified, halide free, concentrated zinc sulphate solution. Cadmium is removed from the solution by cementation. High purity zinc metal is electrowon from the purified solution and sulphuric acid generated is recycled to the process. The leach residue containing zinc ferrite is further treated to recover lead and is finally suitable for disposal.



**Fig. 2 :** Solvent extraction and electrowinning process to treat copper rich zinc secondaries.

**EZINEX Process :** This hydrometallurgical process is based on the leaching of the secondaries with ammonium chloride to solubilize zinc, lead and cadmium oxide. The leach solution is filtered, followed by purification of lead and cadmium by cementation on zinc dust and electrowon to produce high grade zinc metal. The iron rich leach residue containing Zn-ferrite is dried, palletized with coal, and recycled back to EAF, thus no byproducts are produced for disposal.

**CENIM-LNETI Process :** This is based on ammonium chloride leaching of secondaries, followed by solvent extraction and electrowinning / precipitation of zinc. This technique uses integrated processes to prepare various other products and has flexibility to treat different raw materials of variable compositions. The process can be adopted in small and medium scale industries.

## **COPPER**

### **Copper Industries in India**

Until the late nineties, Indian market for copper was mainly dependent on the indigenous primary resources. But the demand for copper constantly outpaced domestic production, and thus the major thrust was upon the imports. The Indian copper industry underwent a drastic transformation since the late-1990s, from an import sensitive industry to a potential exporter, due to globalization through a series of economic and liberalization reforms. As against a very low capacity of 47,500 tpa till 1997, solely owned by public sector Hindustan Copper Limited (HCL), India today has a copper smelting capacity of 847,500 tpa with an overpowering contribution from the private sectors: Sterlite Industries Limited (SIL) and Hindalco Industries Limited (the copper business division is known as Birla Copper). In addition, SWIL Ltd. has started operating its 50,000 tpa plant based on the secondary route. India's import of cathode copper has declined significantly with more than six fold increase in cathode copper production.

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 are produced by small scale units mainly from foundry dross, ash, scales, floor sweepings etc.

### **Recycling/Disposal of copper waste**

Copper as a metal provides least scope for environmental pollution, but the quantity of 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.

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.

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

Other than these wastes generated from the major industries using primary ores/secondary concentrates, Copper waste is also generated as copper scraps during the manufacturing of finished products as cuttings and shredding, from electrical and electronic equipments in the form of used wires, electronic products, personal computers, mobile phones, refrigerators which are used for domestic and even industrial purposes. These discarded materials are rich source of copper and other valuable metals but due to the complex nature of these wastes metal recovery process may be tedious. Other valuable waste is the electrical wires, cables bus bars etc made of copper. Such materials contain very pure copper and thus metal recovery is easier which may be done by pyroprocessing. However recycling this electrical and electronic waste is still not much in vogue because of the lack of proper collection system.

### **Scrap Recycling**

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 are produced by small scale units mainly from foundry dross, ash, scales, floor sweepings etc. It is estimated that about one third of the domestic demand in India is met by secondary copper produced through processing of scraps generated indigenously and those sourced through imports.

In order to keep the environment clean and safe, generation of such wastes need to be treated with the most advanced, commercially and economically viable technology. The scrap recycling industry in India is poised for explosive growth in the years ahead as most of the companies rely heavily on imported scrap material to meet the requirement for their process. According to the Institute of Scrap Recycling Industries, Inc (ISRI), India is one of the fastest growing markets in the world for scrap metal. India ranks fifth after South Korea, Japan, China, and Taiwan among the nations who import scrap for recycling. According to market analysts, the demand is so enormous that India can consume almost any quantity of copper, tin, and brass scrap.

### **Other process waste treatment**

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

Depending upon the metal concentration in the metallic wastes different treatment/ metal recovery processes are opted and wastes such as 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.

During pyrometallurgical production of copper from copper ores about 2.2 ton of slag is generated for every tonne of metal. The slag contains materials like iron, alumina, calcium oxide, silica etc. To avoid dumping / disposal of the slag several attempts have been made to explore the possible utilisation of copper slag all over the world. The favourable physico-mechanical characteristics of copper slag can be utilised to make the products like cement, fill, ballast, abrasive, aggregate, roofing granules, glass, tiles etc. apart from recovering the valuable metals by various extractive metallurgical routes. At present major fraction of slags from the primary copper plants are dumped near the plant or designated area. Hence, its long term effect on water pollution due to leachate generated may not be guaranteed unless it is so proved through toxicity characteristics leachate procedure (TCLP) test.

## ALUMINIUM

### Aluminium Industries in India

Bayer's Process is the only process adopted world wide for the production of aluminium in which substantial amount of red mud is generated. Production of one ton of alumina is accompanied by generation of about 1.0-1.5 tons of redmud. 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 aluminium, which does not generate red mud. Indian alumina plants have 1.692 million tons of annual capacity and generate about 2 million tons of red mud every year.

The major constituents of redmud are 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 titanium oxides. The quantity generated and their chemical composition, collected for each Indian industries are incorporated in Table-2.

**Table 2 : Chemical composition(%) of red mud generated at different plants**

Constituents	NALCO	HINDALCO	MALCO	BALCO	INDAL (Muri)	INDAL (Belgaum)
$\text{Al}_2\text{O}_3$	15.0	17-22.4	14.0-	18.0-20.0	24.0-26.0	18.0-20.0
$\text{Fe}_2\text{O}_3$	62.78	25.6-33.2	18.0	27.0-29.0	36.0-38	40.0-50.0
$\text{TiO}_2$	3.77	15.6-16.5	50.0-	16.0-18.0	16.0-20.0	8.0-11.0
$\text{SiO}_2$	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
$\text{Na}_2\text{O}$	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	-	-	-	-	-
$\text{P}_2\text{O}_5$	0.67	-	1.0-2.0	-	-	-
$\text{V}_2\text{O}_5$	0.38	-	-	-	-	-
$\text{Gd}_2\text{O}_3$	0.01	-	-	-	-	-
LOI	9.50	8.5-12.6	-	12.60	-	10.0

## **Treatment/Disposal of Red mud in Aluminium Industries**

- The red mud is disposed off mainly by dumping in mud lake, dam, and dykes or in a few cases in natural valleys. The major problems of red mud disposal by land fillings are :
- Requirement of huge area. (Unto 1 Sq. km. for 1 million tons per year alumina plant every five year).
- Alkali seepage into ground water resources, and possibility of alkaline rain water run off creating hazards to the crops etc.
- Dust pollution: In the windy and summer season air borne alkaline fine dust creates unhealthy condition surrounding the storage. It is more with dry staking.
- Occasional breach in dykes and aesthetic damage etc.

With the growing concern of environmental protection as well as land conservation, a systematic effort has been made to modify and improve disposal methods. The details of the red mud disposal practices at the Indian alumina plants are summarised in Table-3. Many plants in recent times are practicing dry staking disposal of red mud which required much less land and promoted consolidation and hardening of red mud, consequently resulting in stable and safer deposit. On account of damage to aquatic/marine life disposal into sea or river streams is not in favour.

**Table 3 : Red mud disposal practices at the Indian alumina plants**

<b>Sl. No.</b>	<b>Name of the Plant</b>	<b>Red Mud MT/MT of alumina</b>	<b>Dumping Procedure</b>
1	INDAL, Muri	1.35-1.45	This refinery adopted the closed cycle (wet slurry) disposal system (CCD). The disposal ponds have not been provided with any liner.
2	INDAL, Belgaum	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 Renukoot	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, Korba	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 mesonary and well protected polythene liner and clay layer.

5	NALCO, Damonjodi	1.2	A modified CCD method is used for disposal, subjected to six stage counter current washing by pond returned water (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 semipervious clay with base filters.
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#### Treatment/ Disposal of Spent Pot Lining and Fly Ash

Besides the red mud, other two major solid wastes generated in the aluminium industries are spent pot lining (SPL) and fly ash. Spent pot lining is the waste material dug from the cathodic lining of the electrolysis cells when the cell has failed. It contains sufficient amount of sodium (12-18%), fluoride (12-18%) and a small amount of cyanide (0.1 - 0.3%). About 20 - 40 kg of SPL is generated per tonne of aluminium produced and is mostly stored in the secured landfill. Indal plants were first to treat SPL in the 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 aluminium plants also store the SPL in the designated areas. Some attempts have been made world over to use spent pot lining for 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 our country for such purposes.

Fluorides from aluminium industries contaminate the environment through primary and secondary emissions (1-6 kg/t) and SPL (4-8 kg/t) besides waste water. Scrubbing process and SPL treatment recover a major part of fluoride and it is essential to monitor the waste water to check the fluoride contamination. Huge quantity of fly ash generated in the alumina plant and in captive power station is dumped near the smelters. 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 rest amount is disposed off as waste dumping. A suitable scheme needs to be developed for the meaningful utilization of this resource.

#### TCLP Test

Characterization of the solid wastes for disposal from above industries, for hazardous constituents, needs be stressed to ensure lesser damage to the environment. In this context it is essential to subject TCLP test on all the solid wastes being disposed as prescribed by USEPA (Table-4) to enable least contamination of water table and stream.

**Table 4 :** Limits prescribed for TCLP test on solid wastes as per US-EPA.

SI No.	Contaminants	EPA Hazardous Waste No.	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	5.5

## **CONCLUSIONS**

Effluent and solid waste generated from non ferrous metallurgical industries are more severe as compared to ferrous industries. Generation of these wastes particularly solids even with best intention and effort can not be eliminated. In such cases a complete waste management system should be adopted which must include waste reduction, reuse and recycling in addition to safe disposal methods.

Since there are no limits prescribed in the Indian context for hazardous constituents of leachate in the solid waste disposed, it is difficult to establish their hazardous nature in view of the different type of raw materials and varied composition used in our country as compared to those used in other countries. Hence TCLP tests as per USEPA becomes mandatory to ensure acceptable leachability of the toxic metals and establish these wastes as non-hazardous on disposal.