Environmental & Waste Management
Eds.: A. Bandopadhyay, Rakesh Kumar & P. Ramachandrarao

Clean Technologies in Nonferrous Metals Recycling

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ABSTRACT

The importance of metal recycling is highlighted. A brief overview of technology used in the recycling of common nonferrous metals such as aluminium, lead, zinc and copper is presented. Both traditionally used processes and clean technology options that has emerged in the recent past or are in the development stage are discussed.

Key words : Recycling, aluminium, lead, zinc, copper, cleaner production

INTRODUCTION

Metal recycling or recovery from secondary resources and wastes is closely linked with the concept of *sustainable development* - an idea that has been much in vogue after the 'Earth Summit' in Rio in 1992. Recycling is endowed with several merits, for example, conservation of ore resources, huge savings in energy, and solution to waste disposal problem. Lower energy consumption as compared to primary production, about 5% in the case of aluminium, 6-10% for lead in batteries, 2-5% for magnesium, 20-25% for zinc, about 30% for copper, and 50% for titanium, also results in the conservation of fuel resources and lessen global warming due to minimisation of emissions of green house gases.[1] Thus, it is not surprising that presently out of the total metal consumed, 30-40% Al, 50-60% Cu, 20-30% Zn and 40-60% Pb is recycled in USA, Japan and West Europe. The outlook for recycling varies from one country to another.[2] For example, recycling industry in Europe has a strategic role because of its high dependency on non-EC primary raw materials (often greater than 90%). In USA, metal recycling is carried out to meet demand supply gap and for environmental considerations. In a developing country like ours, the metals recycling industry can thrive largely for making profit. Cu, Pb and Zn can be recycled to fulfil the demand-supply gap, and Al to overcome the energy shortage problem. It is essential that the technologies available in the country are ecofriendly, efficient and fulfil the requirement of recycling economy. In this context, close monitoring of the recent developments is necessary.

In spite of several advantages of metal recycling, it is not free from environmental problems. In the past there have been sustained efforts to develop 'Cleaner Recycling Technologies' that are flexible, efficient, less energy consuming, free from use of harmful substances, minimise waste and emissions and more environmental friendly. The objective of this paper is to review some of these developments with respect to the recycling of common nonferrous metals - aluminium, lead, zinc and copper.

ALUMINIUM

Primary production of aluminium being among the highest, recycling of aluminium is an energetically and strategically favourable proposition. Like other metals, aluminium is used either in pure form (e.g., aluminium foil) or alloyed with other metals. Major sources of recycled metals are high value 'new scrap'. and lower value 'old scrap' which are characterised primarily by the composition and make-up of the material to be recycled. High value processing scrap from off cuts and rejects can usually be returned to the same product. Lower value scrap from used consumer goods and machinery has widely varying composition in terms of elements such as magnesium, zinc, iron, silicon and copper as it may include mixtures of wrought and cast alloys. Typical process flow diagram for aluminium recycling is shown in Fig. 1.

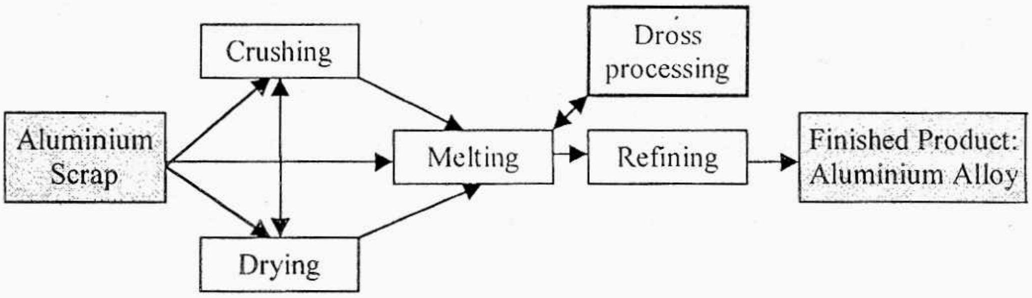

Fig. 1. Generalised process flowsheet for aluminium recycling [3]

The number of steps and exact flowsheet depend on the composition and type of scrap. In cases where sorting and blending are insufficient, used scrap may have to be mixed with primary aluminium or some refining must be carried out. The main method of refining aluminium scrap is chlorination[4-6] in which the principle of refining is the preferential reaction of magnesium with chlorine. Hydrogen removal and inclusion elimination also take place with chlorine gas treatment. Various developments in chlorination include equipment designed to optimise chlorine efficiency and the use of aluminium salts and other fluxes to provide the halogens for reaction. However, there are serious limitations on chlorine refining mainly associated with environmental problems, for example. (i) acid, dust and salt emissions which require expensive exhaust gas scrubbing and waste disposal (ii) operator safety and (iii) plant corrosion problems.

Another method of secondary aluminium recovery uses aluminium drosses as the charge instead of scrap. Traditionally, the term dross was defined as a thick liquid or solid phase that forms at the surface of molten aluminum, and is a by-product of melting operations. It is formed with or without fluxing and the free aluminium content of this by-product can vary considerably. Drosses containing about 30 percent metallics are usually crushed and screened to bring the metallic content up to about 60 to 70 percent. They are then melted in a rotary furnace, where the molten aluminium metal collects on the bottom of the furnace and is tapped off. Salt slags containing less than 30 percent metallics may be leached with water to separate the metallics. The use of AlF_3 rather than chlorine in the demagging step reduces demagging emissions. Fluorides are emitted as gaseous fluorides or as dusts. Baghouse scrubbers are normally used for fluoride emission control.[7]

Recent Developments

In addition to alloying elements, aluminium scrap often includes lacquers, paints and plastic coatings. Alcan Recycling has developed a fluidised bed reactor that can remove such coatings from aluminium scrap containing up to 50% organic material. The aluminium scrap is introduced to a hot (<500°C) fluidised bed of alumina that heats the scrap and oxidises its organic component. The reactor, in operation since 1994, can process 2-8 t/h of scrap, depending on the organic content, and recover over 98% of the metal.[1,8]

The search for alternatives to chlorination as a magnesium elimination process is based on two main principles. One is that magnesium is more electropositive than aluminium and can be removed by fused salt electrolysis processes that are currently receiving research and development attention.[9-12] The other principle is that magnesium is relatively more volatile than aluminum, hence 'demagging' can be accomplished by vacuum treatment. The literature indicates commercial application of vacuum treatment mainly in Europe. In some cases the principal concern is to remove hydrogen[13-16] whereas in others the aim has been to eliminate zinc and magnesium [17,18]. The inherent advantages of vacuum treatment are: (i) environmental problems are solved by avoidance of toxic gases and chemicals (ii) a wider range of metallic solute impurities can be removed and (iii) there is removal of hydrogen gas and non-metallic inclusions. Use of coreless induction furnace for aluminium scrap melting has also been reported in United Kingdom as a substitute for conventional melting practice and energy efficient and ecofriendly technology.[19]

In addition to the classic dross-recycling process based on use of halide based fluxes, a new dross treatment process using a water-cooled plasma gas arc heater (plasma torch) installed in a specially-designed rotary furnace was patented recently.[20] The new process eliminates the use of salt flux in the conventional dross treatment process, and reports recovery efficiencies of 85 to 95 percent.

LEAD

Extensive secondary processing has been a feature of the lead industry. Lead bearing secondaries include: scraped lead acid batteries, cables/rolled/extruded products, oxides/ pigments. Globally, over 60% of the total lead is recycled.[21-23]. Only lead acid batteries, lead cable sheathing or lead sheet and pipe make any significant contribution as recycled old lead scrap. Of these sources of secondary lead raw materials, battery scrap (mainly from automobiles) is by far the most important, accounting for upwards of 70-80% old scrap arising in many countries and perhaps as much as 90% in developed country such as USA.[24] Lead acid batteries are a complex consumer good comprising of lead (70-80%), free acid (12%), polypropylene (5-6%) and separators (and ebonite) (2-3%).[22,25] Lead in the batteries is present in metallic form, as grids, plugs and connections, and as oxide/sulfate. Lead in grids is used as lead alloys and may contain one or more of the following elements : Sb, As, Sn, Se, Cu, S, Cd, Ag, Ca and Al.[26] Many of these elements present in the lead alloy are considered toxic.

Traditional Processing

Traditionally, the processing of lead acid batteries is carried out using pyrometallurgy. Fig. 2 shows the typical flowsheet of a lead batteries scrap processing plant as practised in many advanced countries.

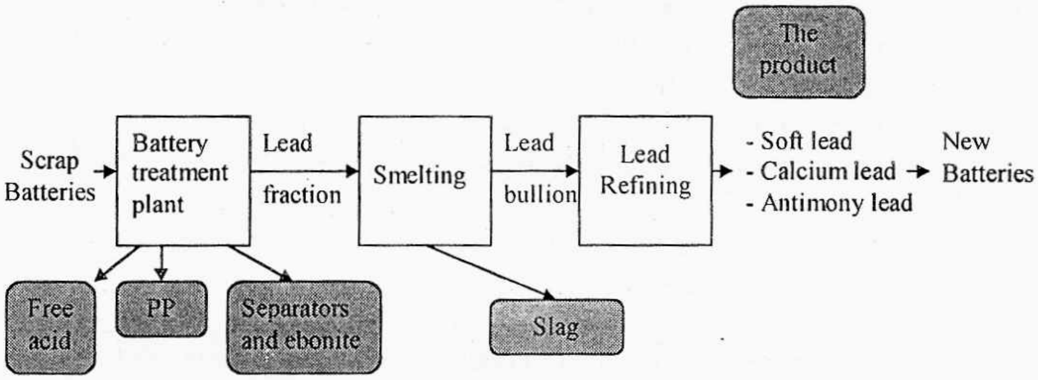

Fig. 2. Typical flowsheet of lead batteries scrap processing plant

Although secondary plants use pyrometallurgical smelting processes similar to those employed at primary smelters, there are key differences in feed materials and the type of smelting furnaces in use. The three key operations achieved during smelting are feed introduction and initial charge ignition, 'sweating' of the charge to release the metallic elements and finally, 'slagging' the charge to separate molten lead from the oxidized impurities. Currently used secondary smelting processes include blast furnace, reverberatory furnaces, short rotary furnace and top blown converters or Kaldos.[24,27] Table 1 summarizes the main features of various pyrometallurgical processes. Many secondary producers use a combination of blast furnace and stationary reverberatory furnaces to make use of the flexibility of the former and refining capability of the later. Rotary furnaces are used on their own, because of their greater flexibility. Well over half of the plants in western world (excluding communist world) use short rotary furnace for smelting. The top blown rotary converter has successfully treated scrap batteries charged directly without breaking and plastic separation at Boliden's Ronnskar Works in Sweden.[27] Electric arc furnace technology is in use on a limited scale, normally to remove lead from secondary blast furnace slags.[27] Sulfur dioxide and particulate emissions in the off-gas and slag disposal are the main environmental issues in smelting.

Development in Traditional Processing

The use of non-metallic constituents of the battery, like casing etc, as fuel during smelting is discouraged. Current emphasis is more on the separation of all the constituents and this is the crux of cleaner technology in the recycling. Battery breaking and the feed preparation is the first operation in most plants. Some of the patented technologies available for this purpose are: Tonolli, CX (from Engitec), Stolbergen, Penarroya, etc.[28] Although there are major differences both in techniques employed and the level of sophistication of equipments in the available technologies, segregated streams of battery grid metal, battery paste, polypropylene, rubber and waste acids are produced in each case through a sequence of crushing, screening/washing, heavy media separation and flotation processes. In some cases, battery paste is treated with sodium carbonate to convert lead sulphate into lead carbonate (desulphurisation) and, consequently, minimize sulphur problem in the smelting operation.[28,29]. Conventionally, the battery acid (sulphuric acid) has been chemically neutralized and then disposed of in the hazardous waste dumps, but more modern battery breaking processes allows the conversion of acid (and sulphur from battery paste) to sodium sulphate salts, which can be sold. In the recent past, considerable progress has been made in some of the developed countries in automation and mechanized handling of battery scrap.[24]

Table 1 : Main features of secondary lead smelting processes[22,23,27,28]

Process	Smelting/ Mode	Features/Current Status
Blast Furnace	Shaft/ Continuous	• Can be used for a range of secondary feed – scrap lead, slags, drosses and flue dust • Widely used worldwide • Inherently dirty technology producing high silica mattes and slags
Reverberatory Furnace	Bath/ Continuous or Batch	• Used primarily for high oxidic and antimony containing feed • Widely used worldwide • Environmental problems
Short Rotary Furnace	Bath/Batch	• Used primarily for high metallic feed • Widely used worldwide • Produces a reactive soda slag which can cause disposal problem
Top Blown Rotary Converter	Flash orBath/ Batch	• Used for smelting residues and scrap including unbroken batteries • In operation in Sweden on secondary feed
Electrothermic Furnace	Bath/Batch	• Use metallic and oxidic feed • Russian companies offer the technology • Costly equipments • Status not known

Integration of a modern battery breaking and feed preparation plant with the smelting operation is helpful in minimizing particulate emission. Gradual feeding of the rotary furnace, in sharp contrast to one-time feeding and ignition of charge, can minimize particulate emissions in a short rotary furnace. Emission level of SO_2 in the off-gas is reduced through desulphurization of the battery paste prior to feeding into smelting furnace. However, feeding of desulphurized paste result in active soda slag that poses disposal problem. An alternative approach, that involves feeding of iron scrap to fix sulphur in the furnace as iron sulphide matte, is practiced in some plants. Use of oxygen during smelting, to reduce off-gas volume, is practiced to minimize particulate emissions.[29] In addition to the measures adopted during smelting for pollution control, treatment of off-gas is important to further control the levels of lead bearing particulate emission and SO_2 gas. The gas handling practice may vary from plant to plant. Typically, gas handling may involve cooling (using waste heat recovery, forced draft cooling etc.), removal of particulate emissions by bag-house filters, electrostatic precipitators, etc., and finally neutralisation of gas, for example, using lime solution in a venturi scrubber.[22,23,27-29]

The dezincing operation is particularly critical for secondary producers, given the detrimental effect of zinc as an alloying element in lead products. Antimonial lead, traditionally the most common product of secondary operations given its importance in battery grid manufacture, is obtained directly following decopperising and softening (arsenic and tin removal) processes. Calcium lead alloys and lead oxide are both normally made from softened lead. Calcium is added in its metallic form or as calcium carbide. Lead oxide is prepared by Barton Process that involves atomisation of molten lead and its oxidation. The purity of lead used for oxide is more important than the metallic used for grids etc otherwise it will lead to 'gassing' in the maintenance-free batteries.[24]

Hydro- and Electro- metallurgical Processes

The increasing environmental pressure exercised during the last 20-25 years, on both primary and secondary lead facilities, has stimulated the research of new, more environmentally friendly technology, based on hydrometallurgy and elctrometallurgy approach, as an alternative to pyrometallurgy. Considering the high electrochemical equivalent of lead, these alternative technologies make it possible to couple the environmental requirements to the energy savings with substantial reduction of production costs compared to the traditional processes. These processes are described and analysed in recent articles by Prengaman[30] and Diaz and Andrews.[31,32] Although different in some aspects, the more advanced processes such as USBM, RSR, Engitec CX-EW (or EWS) and Placid, are based on the same philosophy, which include following main steps:

a) Conversion of insoluble $PbSO_4$ and PbO_2 into leachable products - $PbSO_4$ is converted into soluble lead carbonate, hydroxide or sulfide using alkali/ ammonium carbonate, sodium hydroxide (RSR, USBM, CX-EW processes) and solution of sodium sulfide and sulfuric acid (CX-EWS process). In the CX-EWS process, sodium sulfate formed as the by-product is reduced with carbon to regenerate Na_2S. Reduction of PbO_2 is carried out using lead powder, hydrogen peroxide, SO_2, alkali sulphites or by a thermal system.

b) Leaching by a suitable electrolyte to put the lead ions into solution - commonly used leaching medium are fluosilicic/fluoboric acid (RSR, USBM, CX-EW processes), ferric fluoborate (CX-EWS process) and HCl brine solution (Placid process) etc.

c) Lead electrowinning with an insoluble anode with oxygen evolution except in CX-EWS process. The electrowinning practice in different processes is compared in Table 2. Anode material has been an important area of research in the development of an electrowinning cell. The CX-EWS and the Placid processes make use of advanced electrowinning cell technology based on ion-selective membranes. A new $PbSO_4$ slurry process[30] uses fluidized bed electrowinning cell in conjunction with ion-selective membrane.

It is likely that a full scale lead electrowinning plant will be operational in near future. Hydro- and Electro- metallurgy based plants are primarily suitable for treating lead paste. Integration of these process with pyrometallurgical processes has been suggested, for example in the case of Placid process, to make battery scrap processing more environmentally friendly through effective elimination of atmospheric lead emissions.[31]

Table 2 : Comparison of the electrowinning processes [31].

Process	Electrolyte	Additives	Pb (g/l)	Purification	Cell type	Current
RSR	Fluosilicic /Fluoboric acid	>500 ppm As & boric acid	70-200	None	Simple	100-200
USBM	Fluosilicic acid	3-6 g/l H_3PO_4 +0.05 g/l bone glue + 4 g/l lignin sulfonate	25-150	None	Simple	150-250
Engitec	Fluoboric acid	Glues	50-100	None**	Composite anode#	320
AAS*	AAS	None	-	None	Cascaded	-
Placid	HCl Brine solution	None	25	Cementation	Ion-selective membrane	1200

*Ammonical ammonium sulfate leaching

**For CX-EW process, cementation is used in CX-EWS [28]

#CX-EWS process uses graphite anodes with additives to prevent formation of PbO_2 [24]

ZINC

Globally, over 2 million tonnes or 30% of zinc supplies come from secondary or recycled zinc. The contribution of different secondary sources of zinc for recycling include: old/new brass scrap (32%); old/new diecasting scrap (16%); old/new zinc sheet (10%); galvanizing residues (23%) and flue dust from steel plants (8%); and miscellaneous sources (11%).[33] Zinc present in brass is recycled as such since any other method would be uneconomical. Diecasting scrap and zinc sheet scrap is either directly melted (if known origin) or used in the production of zinc dust and zinc oxide. The focus here is primarily on solid residues from galvanizing industry (dross of different kinds, zinc ash or skimmings, flux skimmings), electric arc furnace dust (solid wastes) and spent acid from galvanizing plant (liquid effluent). Effective elimination of various toxic elements, such as Cl, Cd, Pb etc., from the waste, in particular EAF dust (Table 3), is a prime technological challenge in zinc recycling from the point of view of clean technology development.

Table 3. : Typical composition of electric arc furnace dust, wt.%[28]

Zn	Pb	Cd	Cu	Sn	As	S	Cl	F	FeO	CaO	SiO_2
16-38	2-7	.01-0.1	0.2-0.4	0.2-0.3	.05-0.1	1.5-2.5	1.5-2.5	0.1-0.2	25-35	5-10	3-5

Zinc Bearing Solid Wastes

The generalised scheme involved in the recycling of zinc bearing solid wastes is shown in Fig. 3.

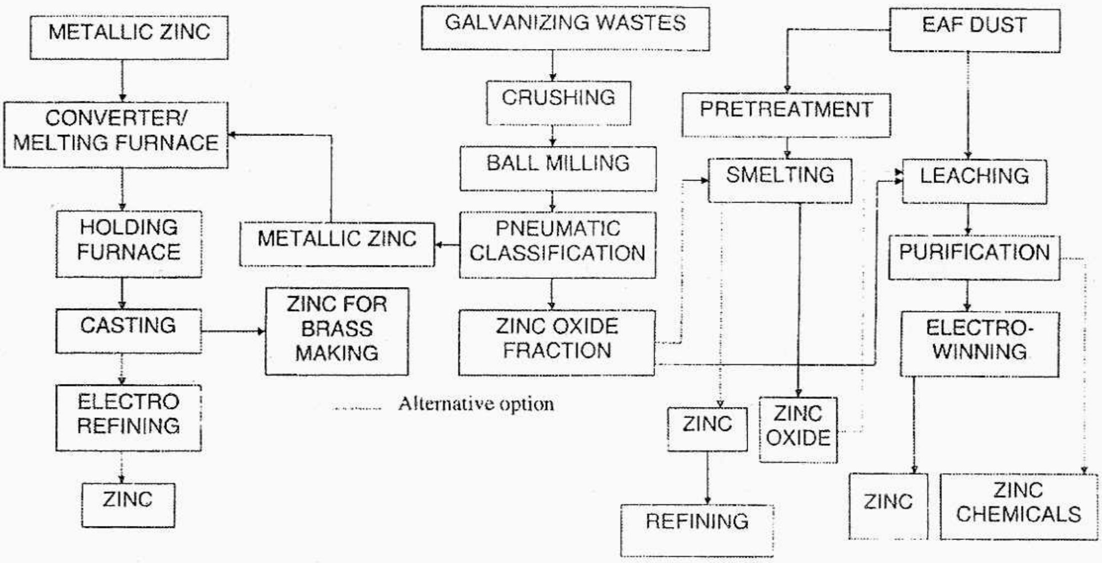

Fig.3 : Generalised flow sheet for the recycling of zinc bearing solid wastes

Typically, the recycling process is composed of crushing and physical separation to recover metallic and nonmetallic (oxidic) fractions, and melting process to melt the metallic zinc. The selection of process depends on the complexity of the waste. Flux is added during melting to prevent oxidation and minimize melting losses. In some cases, metallic zinc is electrorefined. As listed in Table 4, a pyrometallurgical process or a combination of hydro- and electro- metallurgical processes is used for the processing of galvanizing residues to produce either metallic zinc or zinc oxide.[22,23,28,34]

Table 4 : Processes for the treatment of zinc residues[22,23,28,34]

Pyrometallurgy	Hydrometallurgy
High zinc contained	Modified Zincex process
Electrothermic process	Ezinex process
Medium zinc contained	Hematite process
Imperial smelting furnace (ISF)	Cebedeau-caustic leach process
Low zinc residues	Cenim-Leneti process
QSL	
Waelz	
SKF Plasma, Mintek Enviroplas, Tetronic, and Electrothermic processes	

Waelz kiln or its variants are extensively used in the pyrometallurgical treatment of zinc residues. In the case of EAF dust, 76% of the total EAF dust is treated by Walez kiln in USA, Japan and Europe. The process yields impure zinc oxide that is used as a feed in Imperial Smelting Furnace, that can accept feed containing upto 36% zinc as secondaries comprising of primarily Walez oxide.[28]

Significant developments has taken place in pyrometallurgical processing of secondary zinc and residues, for example cyclone smelting (Contop process), plasma arc based technology (Enviroplas process of Mintek) etc. Plasma based technology in the processing solid zinc wastes, like EAF dust contributes small fraction in the overall scenario (~ 5%), however, this is receiving increasing attention. Modified Zincex process (developed as a part of EC research programme on recycling) and EZINX process (developed at Engitec, Italy) are important developments in the hydrometallurgical processing of zinc waste.[28,34] The modified Zincex process is based on sulphuric acid leaching of the residue and electrowinning. The EZINX process is based on ammonium and alkali chloride leaching and electrowinning. Zincex as well as EZINX process incorporate a solution purification scheme involving precipitation, cementation and solvent extraction. These processes can effectively tackle impurities such as Cd, Cu, Sn, Pb, Ag, Fe etc., in the feed. It is expected that full scale commercial plants based on these processes will come into existence soon.

Fe/Zn Acids from Hot Dip Galvanising

Hydrochloric acid pretreatment is the most common method throughout the world to achieve a clean surface on steel during galvanizing. Significant concentration of zinc, usually 5-10 g/l but sometime may be as high as 150 g/l, is present in the acid after the pretreatment. Typical composition of the acid after pretreatment is given in Table 5.

Table 5. : Spent pickling acids: typical composition HCl-based baths[35]

Constituent	Concentration
Fe (as $FeCl_2$)	80-150 g/l
Zn (as $ZnCl_2$)	5-150 g/l
HCl	10-80 g/l
Other heavy metals (Cu, Ni, Cr, Mn, Pb, Co,...)	ppm range
Organics inhibitors, oil & grease	< 0.1 g/l

The zinc in the spent acid must be recovered to decrease the disposal costs for the spent mixed acids and obtain zinc metal as a valuable product. More than 35,000 tonnes of zinc is recovered every year from spent acids generated during hot dip galvanizing.[33] Various treatment routes[36] used/examined for spent hydrochloric acid pickling solutions are summarized in Table 6 and the advantages and disadvantages of different treatment routes are indicated.

Table 6 : Treatment routes for spent hydrochloric acid pickling solutions

Treatment route	Comment(s)
A. Routes without Zinc Separation	
Spray roasting	✠ high investment cost
Electrolysis/ Electrodialysis	✠ economic problem in treating the Cl2 gas evolved
Retardation	✠ utilizes resin to separate dissolved salt from free acid ✠ process is of relevance for active pickling bath ✠ salt removal not selective
Neutralization/ Precipitation	✠ most common method ✠ selective $Zn(OH)_2$ precipitation not possible ✠ chloride content of the wet sludge prohibits further use
Evaporation	✠ impure quality of product ✠ specialized corrosion resistant equipment
B. Routes with selective zinc removal	
Fixed bed ion-exchange	✠ ion-exchange resins are very sensitive to contamination ✠ a large volume of expensive resin is necessary
Solvent extraction	✠ solvent, like trioctyl amine (TOA), tributyl phosphate (TBP), has been successfully used ✠ several advantages - high throughput with compact equipment - flexible process with continuous close circuit operation - clean valuable product solution (with $ZnCl_2$ post-treatment) ✠ a mobile plant concept has been proposed

COPPER

Recycling of copper and copper alloys scrap is an important part of copper metallurgy and, at present, copper recycling rate amounts to about 40% of the production worldwide.[37-39]

Conventional Processing

The copper content, type and levels of impurities present and, as well as, complexities of the scrap are dependent on its origin. Typically in the case of recycling of shredder scrap from automobiles, a shredder fraction contains not only copper metal but also metal like Zn, Sn, Pb and Ni. Copper can be present in this fraction in pure metallic form, as alloys, for example brass and bronze, and in physically joined form with other metals. Today's processes of metal recovery from copper and copper alloys scrap consist of several pyrometallurgical steps.[37-44] The melting of scrap, for example, in converters of primary smelters or anode furnace of primary or secondary refineries (where large portions of impurities, for example, Al, Fe, Zn, Si, Sn, are removed by oxidation), is well established. Air pollutants are generated during the drying of chips and borings to remove excess oils and cuttings fluids and causes discharges of large amounts of dense smoke containing soot and unburned hydrocarbons. These emissions can be controlled by bag-houses and/or direct-flame afterburners. Usually, the refining of cast anode is carried out electrolytically at the end in a sulphate bath. The positive aspects of the current practice are relatively moderate sensitiveness upon the constitution of scrap and a bright electrolytic copper as the end-product. Main disadvantages of the process are relatively high specific energy consumption and recovery of only copper from secondary raw materials of complex constitution. The pyrometallurgical unit processes have a major impact on the cost of the final product because they consume nearly 50 percent of the energy involved in the overall process. The valuable elements are removed in slag phase during smelting/refining, elutriated with the flue gases or separated in the slimes generated during electrolysis. Recovery of valuable elements from these waste materials, like slags and slimes, is scarcely carried out due to high expenditures involved.

Recent Developments

There is a need to develop cleaner, more energy efficient and comprehensive process with minimum number of stages, in contrast to the prevailing process, for simultaneous recovery of most of the valuable metals present in a complex scrap. Several new developments have taken place recently with regard to hydro- and electro-metallurgical processing as summarised in the following paragraphs.

Direct electrorefining of scrap in sulphate solution using anode support system is environmentally and economically very attractive as shown in Fig. 4 and processes based on stainless steel or titanium anode system are being developed/used industrially in Chile. Direct electrowinning has been suitable only for high quality (>95% Cu) low volume scrap.[45]

Hydrometallurgical processes using leaching, purification of leach liquor and

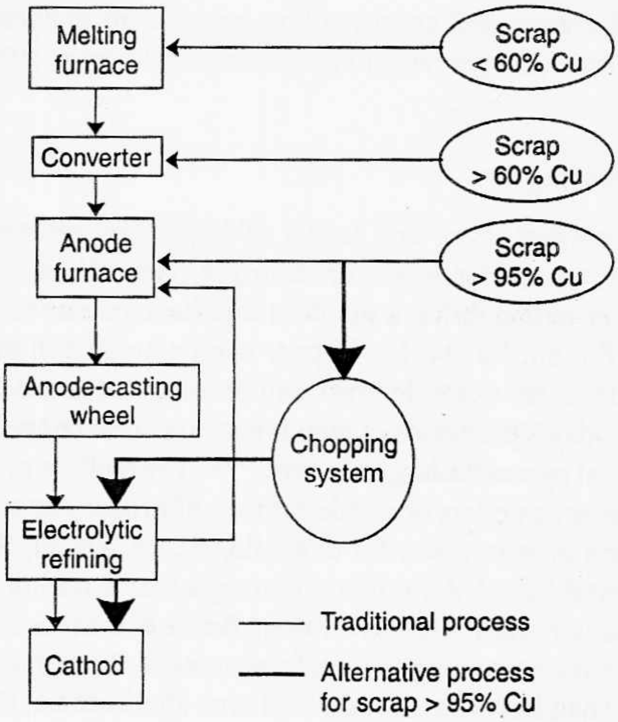

Fig. 4 : Refining of copper by traditional and alternate process for scrap copper [45].

electrowinning have hitherto acquired importance only for the processing of large deposits of low grade oxidised copper ores.[46] Modern unit processes like ion-exchange and solvent extraction are used for the purification of electrolyte and for the enrichment of copper content in the leach solution.[46-48] The end step of the process is almost always electrowinning from a sulphate electrolyte. In order to meet the electrolyte requirement, a sulphate leaching is usually necessary. The sulphate leaching requires use of oxygen as means of oxidation and higher temperature to attain satisfactory leaching rate. In the electrowinning of copper from sulphate electrolyte, deposition of copper takes place at cathode via a two electron process from Cu(II) with a simultaneous and continuous evolution of oxygen at anode. This evolution of oxygen results in a higher electrical energy consumption due to a very large electronegative anode potential (the electrical potential needed for industrial copper electrowinning is ~ 2 V as compared to 0.3 V for electrorefining).[46]

Published literature on the use of non-sulphate solvents for the leaching of copper from ore and/or scrap is very limited.[49] In principle, the use of Copper(I)-bearing electrolyte for the electrowinning permits a 50% saving in electrical energy on the basis of superior electrochemical equivalent. Savings of about 50% in the electrorefining of copper and 500% in the electrolysis of Cu_2SO_4 or CuCl, rather than $CuSO_4$, are reported.[50,51] High concentration of Cu(I) can be solubilized as the $CuCl_2^-$ complex ion in brine solution. Organic nitriles and a variety of other ligands like CO, $CH_2{=}CH_2$, NH_3 also stabilize Cu(I) in solution. Electrolytic recovery of copper via one electron process is established on technical scale only for the electrolysis of chloride-bearing electrolytes.[52-54] An additional energy saving is possible if, instead of the evolution of chlorine, an electrochemical regeneration of leaching medium can actually take place on anode. This is described, for example, for chloride electrolyte [anodic oxidation of Cu(I) by Fe(III)],[50-54], as well as for iron fluoborate electrolyte.[55,56] In addition, halogen (Cl^- and Br^-) complexes (referred to as HALEX) have been utilised for the storage of anodic energy that will not contaminate cathode product. [54]

CONCLUSIONS

In this paper we have made an attempt to summarise global efforts/developments towards Clean Technology for the recycling of common metals – aluminium, lead, zinc and copper. In India, a significant fraction of demand for these metals is met through recycling. The scale of operation of recycling plants in India is small or tiny as compared to the advanced nations. Implementation of sophisticated technology at small scale of operation is not easy. It is not surprising that the recycling industry is in a disorganised state. Information pertaining to quantum of recycled metals is scanty or missing altogether. In order to correct this scenario, the Ministry of Mines and Minerals (MoM) has taken an initiative to create a national forum to promote recycling of nonferrous metals in our country through environmentally friendly technologies. The form is to include all the stakeholders in the country, including primary producers. There is an urgent need to evaluate clean technology options in the Indian context and chalk out a plan for the industry. The evaluation process needs to concentrate not only on the technical and environmental aspects but has to focus on scale of operation and economic and societal aspects. National Metallurgical Laboratory, with it long experience of working in the area of recycling and waste minimisation in metallurgical industry is making an earnest effort in meeting the objective of the forum set-up by the MoM.

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