

## LEAD ZINC EXTRACTION PROCESSES

K. K. SAHU AND A. AGRAWAL

Email : kksahu@nmlindia.org, archana@nmlindia.org

### INTRODUCTION

Zinc and lead are the two most widely used non-ferrous metals after aluminium and copper as vital materials in everyday life. They are mined and smelted in many countries in both the developed and developing world. Both pyrometallurgical as well as hydrometallurgical methods are used for production of lead zinc depending on the type of raw material used as a charge. In the pyrometallurgical process, ore concentrate containing lead, zinc, or both is fed, in some cases after sintering, into a primary smelter. Lead concentrations can be 50-70%, and the sulfur content of sulfidic ores is in the range of 15-20%. Zinc concentration is in the range of 40-60%, with sulfur content in sulfidic ores in the range of 26-34%. Ores with a mixture of lead and zinc concentrate usually have lower respective metal concentrations. During sintering, a blast of hot air or oxygen is used to oxidize the sulfur present in the feed to sulfur dioxide ( $\text{SO}_2$ ). An increasing proportion of the supply of both metals (over 50% for lead and 30% for zinc) is being met by recycling. Consumption is predominantly in industrialised countries but is increasing rapidly in the developed world.

### LEAD EXTRACTION PROCESS

The principal consumption of lead is for lead-acid batteries which are used in vehicles, industrial batteries, computers, power systems as well as in compounds in the glass and plastics industries and for radiation shielding. Average end use patterns over the last five years are given below.

Batteries	: 71%	Pigment	: 12%
Cables	: 3%	Rolled Extrusions	: 9%
		Ammunition	: 6%

### Primary Lead Processing

The most important lead ore is galena (lead sulfide). Other important ores such as cerrusite (lead carbonate) and anglesite (lead sulfate) may be regarded as weathered products of galena and they are usually found nearer to the surface. Lead and zinc ores often occur together and for most extraction methods they have to be separated. The most common technique is selective froth flotation. The ore is first processed to a fine suspension in water by grinding in ball or rod mills. Air is then bubbled through this pulp in presence of various chemicals and proper agitation, the required mineral particles become attached to the air bubbles and are carried to the surface to form a stable mineralized froth which is skimmed off. The unwanted or gangue particles are unaffected and remain in the pulp.

## Conventional Blast Furnace Process

The conventional pyrometallurgical primary lead production process consists of four steps: sintering, smelting, drossing, and refining (Fig.-1). A layer of mixture of concentrate, flux and some returned fines is moistened and ignited. Sulfur in the mixture provide the fuel for the exothermic reaction and rapidly propagated by a current of air. In the process, sulfide is largely converted to oxide and fine powder and agglomerated into lumps. The sintering feed, along with coke, is fed into a blast furnace for reducing, where the carbon also acts as a fuel and smelts the lead-containing materials. The molten lead flows to the bottom of the furnace, where four layers form: "speiss" (the lightest material, basically arsenic and antimony), "matte" (copper sulfide and other metal sulfides), blast furnace slag (primarily silicates), and lead bullion. All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag, which contains zinc, iron, silica, and lime, is stored in piles and is partially recycled.

The lead bullion is refined using pyrometallurgical methods to remove any remaining nonlead materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as oxides of antimony, arsenic, tin, and copper). The lead is refined in a cast-iron kettle in five stages. First, antimony, tin, and arsenic are removed. Next, gold and silver are removed by adding zinc. The lead is then refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium, which combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step, caustic soda, nitrates, or both may be added to remove any remaining traces of metal impurities. The refined lead will have a purity of >99.9%.

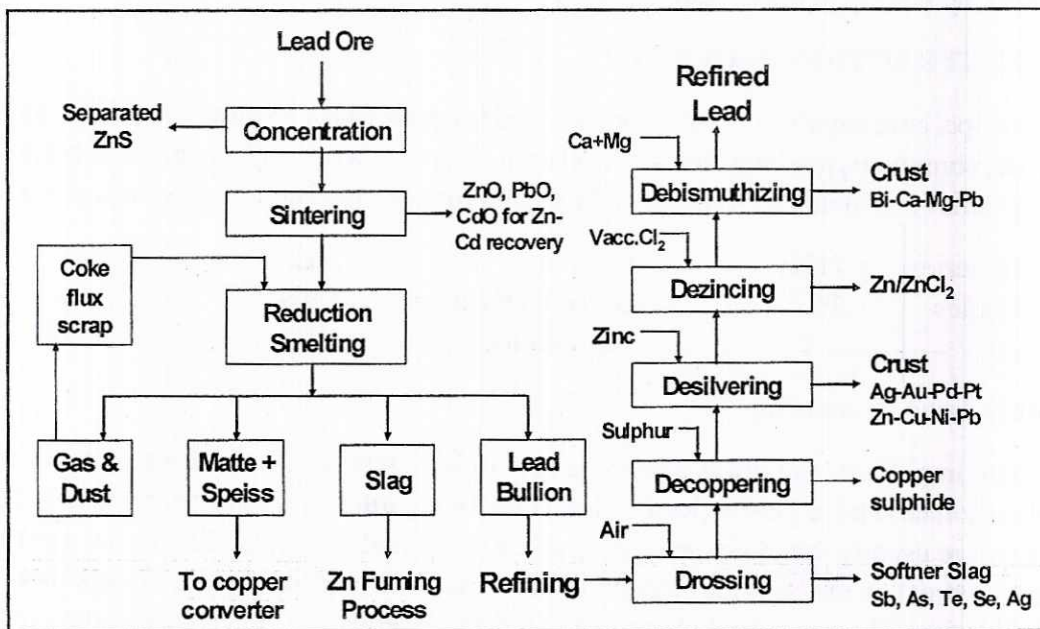


Fig.-1 : Flow-sheet for recovery of lead from lead ore

## Direct Smelting Processes

Keeping in mind the environmental problems and inefficient use of energy, most of the efforts gone at devising processes in which lead is converted directly from the sulfide to the metal

without any need to produce lead oxide in an initial step. Direct smelting processes offer several significant advantages viz. (i) Minimise environmental pollution due to less creation of dust (ii) considerable fuel saving due to effective utilization of heat during the smelting operation (iii) higher concentration sulfur dioxide off-gas is more suitable for sulfuric acid manufacturing. However, the major difficulty in all direct smelting processes lies in obtaining both a lead bullion with an acceptably low sulfur content and a slag with a sufficiently low lead content for safe disposal. In several cases further treatment of either the crude bullion or the slag (or both) is required in a separate operation. There are several direct smelting processes which come close to meeting the desired criteria briefly described below.

**The Kivcet process :** The Kivcet process which originated in the USSR is a direct smelting process in which zinc can be recovered simultaneously with lead. The process is suitable for treating complex ores with high zinc contents. Sulfide concentrate and flux are mixed and injected with technically pure oxygen through a burner into the top of a smelting shaft. The material is roasted and smelted while in suspension forming a mixture of lead and zinc metals and oxides which enter the melt at the bottom of the shaft. Provided the sulfur content of the feed is greater than 18%, smelting is autogenous and no additional fuel is required. The process waste gas containing 40% or more sulfur dioxide passes up a gas cooling shaft, is de-dusted by means of electrostatic precipitation and fabric filters and is then used for sulfuric acid manufacture.

**The QSL process :** The QSL Process was developed in Germany by Lurgi. Sulfide concentrate, return flue dust and flux are continuously mixed with a little water and compacted into pellets which are dropped directly into the oxidation zone of the reactor. The pellets dissolve rapidly in the resulting molten bath and are partially oxidised to lead and lead oxide by submerged injection of oxygen. Oxidation is autogenous at the operating temperature of 950 - 1000°C and the evolution of lead fume is low.

Metallic lead containing copper and silver sinks to the floor of the reactor and the bullion is tapped continuously. Lead oxide and other metal oxides form slag which flows to the opposite end of the vessel where it is continuously discharged. On the way it passes over a series of submerged injectors through which powdered coal is blown. This reduces the lead oxide to metal which sinks to the floor and flows counter current to the slag back to the oxidation zone where it is tapped together with the directly produced primary bullion. The lead content of the slag decreases from about 55% in the oxidation zone to less than 2% in the slag leaving the reactor. The sulfur content of the lead bullion is about 0.3%.

**The Isasmelt Process :** The Isasmelt process for lead is a fully continuous two stage process which is based on gas injection into melts via a top entry submerged Sirosmelt lance. Submerged injection produces turbulent baths in which high intensity smelting or reduction reactions may occur. In the first stage of the process, lead concentrate is added directly to a molten slag bath and is oxidized by air injected down the lance. Simultaneously, the high lead slag from this furnace is continuously transferred down a launder to a second furnace and reduced with coal. The crude lead product and discard slag are tapped continuously from the reduction furnace through a single taphole and separated. The innovative feature of the Sirosmelt lance

is the use of helical vanes to impart a swirling motion to the process gas stream, leading to an increased heat transfer rate from the lance to the process gas and the formation of a frozen slag layer on the outer surface of the lance. This slag coating protects the lance, so that it can be immersed in the bath for extended periods without excessive wear.

**The Outokumpu Process :** The Outokumpu Flash Smelting process consists of drying, flash smelting, slag cleaning and gas handling equipment. The lead concentrates and fluxes are mixed, dried and is fed into the concentrate burner located on the roof of the reaction shaft. This specially designed burner mixes the feed materials with process oxygen or oxygen enriched air. The concentrate is oxidised and smelted directly into lead bullion and slag - the thermal energy for the smelting of the charges is provided by the exothermic oxidation reactions of the concentrate. The degree of oxidation can be well controlled and thus the quality of the lead bullion, especially the sulfur content, can be regulated.

The potential environmental advantages of the above direct processes are (i) simple control and operation (ii) low dust and fumes emissions, (iii) better control of oxidizing or reducing atmosphere (iv) use of oxygen produces low gas volumes and a high concentration of SO<sub>2</sub> in the off gas which is suitable for sulfuric acid manufacture.

### 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 sulfuric 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.-2). 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 pests are processed separately in a rotary smelter.

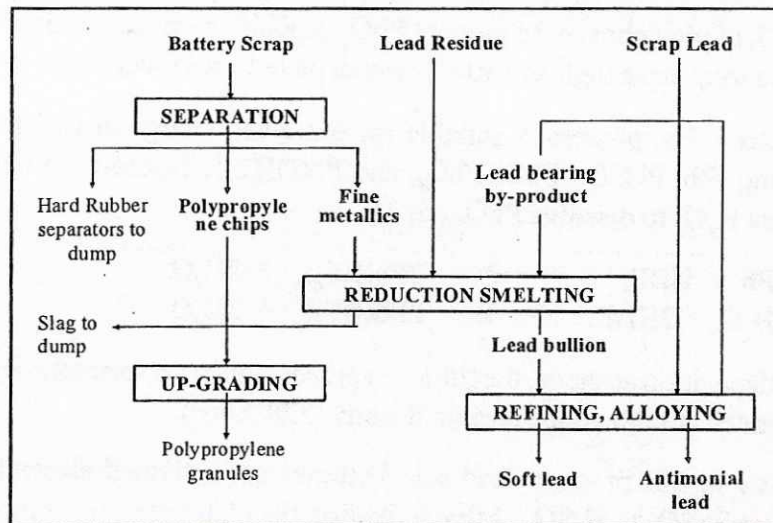
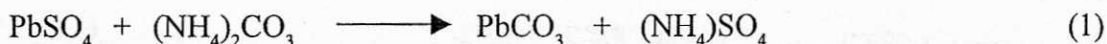


Fig.-2 : General flow-sheet for recovery of lead from spent batteries and other secondaries

### 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 sulfur as a harmless sulfate and to put the lead into a suitable solution for electrolytic recovery. Most processes recirculate leach solutions and produce a high purity lead. Examples of these include the Ledchlor process, which can be used on primary materials. Others hydrometallurgical processes mainly suitable for processing battery scrap are described below.

**RSR Process :** In this process the  $PbSO_4$  portion of the battery sludge is treated with ammonium/alkali carbonate to produce lead carbonate and ammonium sulfate.

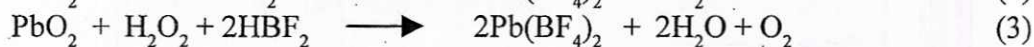
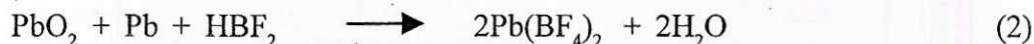


Insoluble  $PbO_2$  part of the sludge can be reduced to soluble form by the addition of  $SO_2$  to an alkali/ammonium carbonate producing alkali sulphite/bisulphite which reacts with  $PbO_2$  to produce  $PbSO_4$ . Sulphite/bisulphite is oxidised to sulfates and lead is precipitated as  $PbCO_3$  or  $PbCO_3 \cdot Pb(OH)_2$ . Alternatively the battery sludge can be heated to  $290^\circ C$  in presence of an organic. The treated sludge is leached in  $H_2SiF_6$  and  $HBf_4$  followed by electrolysis to recover lead.

**Bureau of Mines Process :** Like RSR process the sludge (containing  $PbSO_4$  and  $PbO_2$ ) is pre-treated with ammonium carbonate to desulfurise  $PbSO_4$ . Here the reduction of  $PbO_2$  to  $PbO$  is done by addition of metallic lead powder during leaching with  $H_2SiF_6$ . The drawback of this process is the requirement/recycling of large amount of powder lead, as the  $PbO_2$  content in the sludge is about 35-40%. This process utilises  $PbO_2$  coated titanium anodes and lead cathodes

and about 1-2 g/L of phosphorous to prevent  $PbO_2$  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 desulfurised sludge containing  $Pb$ ,  $PbCO_3$ ,  $PbO$ ,  $PbO_2$ , and  $Pb(OH)_2$  is leached with  $HBF_4$  (eq 2). The process also uses  $H_2O_2$  to dissolve  $PbO_2$  (eq 3).

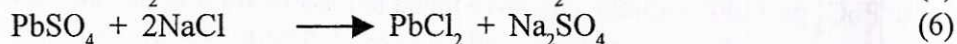
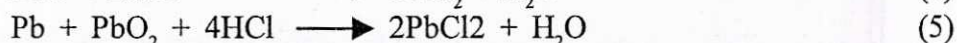
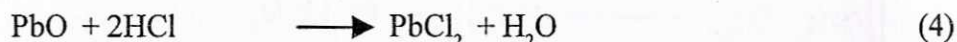


To avoid  $PbO_2$  deposition at anode, the Engitech process utilises a specially designed composite anode, that operates at high anode current density ( $320 \text{ A/m}^2$ ).

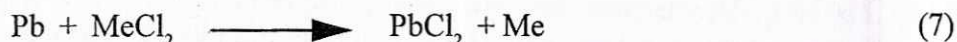
**Ginata Process :** In this process lead acid batteries are activated electrolytically in dilute  $H_2SO_4$  to convert  $PbSO_4$  to  $H_2SO_4$ . After activation the plates are short circuited in fluoboric acid electrolyte where lead is oxidized and dioxide is reduced with the formation of highly 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 sulfate (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 desulfurisation 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 electrowinning. 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.

## Lead Industries in India

India has two major primary lead producers namely Hindustan Zinc Ltd (HZL) with Visakapatnam plant producing 22,000 tons per year, Chanderia plant in Rajasthan with an annual capacity of 35,000 tons, and HZL Tundoo plant in Bihar producing 8,000 tons per year with a total of 65,000 tons per year by all the three plants. 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. The Indian Lead Limited (ILL) with a capacity of 24,000 tons per year which is gradually shifting to the concentrate route due to the restricted availability of lead scrap. 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.

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 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.

## ZINC EXTRACTION PROCESSES

Zinc is very effective in protecting steel against corrosion by galvanizing. The ability to die cast complicated components makes zinc indispensable in a multitude of industry and household products. It also has important markets in the brass and construction industries and in chemicals and constitutes an essential nutritional element. The main end uses of zinc are given below.

Galvanizing	: 47%	Semi Manufactures	: 8%
Brass & Bronze	: 19%	Zinc Alloys	: 14%
Chemicals	: 9%		

## Primary Zinc processing

The most important raw material for production of zinc is Zinc Sulfide (ZnS) ore commonly known as Sphalerite. Next in the importance are zinc carbonates (Calamine/Smithsonite) and zinc silicate. Most of the zinc production worldwide originates from sulfide ores. The principal

processes by which zinc is extracted from its ores can be categorized under pyro-metallurgical processes and hydro-metallurgical processes.

### ***Pyrometallurgical Processes***

Presently about 15-20% of the world's zinc production comes from pyro-metallurgical route. The zinc production by horizontal and vertical retort processes and electrothermal process is becoming insignificant due to high power consumption and low recovery. The only pyrometallurgical process of importance presently is Imperial Smelting Process (ISP).

**Retort Process :** The dead roasted zinc oxide is smelted with coke in the horizontal retort furnace. Zinc is produced at about 1000°C in gaseous form by reduction with CO. The zinc vapour produced is condensed in a reducing atmosphere. Therefore zinc oxide reduction with coke is conducted inside a retort which is usually heated externally and prevents oxidation of CO to CO<sub>2</sub>. The zinc vapour is collected in a liquid zinc bath. The principle for production in both horizontal and vertical retort is same. However the latter one can be operated on a continuous basis with zinc oxide and coke charged at the top of the retort.

**Imperial Smelting Process :** Currently about 8 -10% of the world's primary - zinc production are through the Imperial Smelting Process. The process co-produces lead bullion in addition to zinc metal using a mixture of lead and zinc concentrates or complex lead-zinc concentrates as raw material. The ZnO and PbO sinter mix is charged with preheated coke and lime stone in to ISF which provide simultaneous reduction of both PbO-ZnO mixture. The liquid lead bullion is collected at the hearth of the furnace and zinc vapour is rapidly condensed at the top by spraying liquid lead at 600°C. Due to the solubility difference between the two molten metals with gradual cooling up to 400°C, zinc metal separate out from lead.

### ***Hydro-Metallurgical Process***

**Roast Leach Electrowining Process :** About 80% of world's total zinc output is produced through conventional hydrometallurgical route i.e. Roast-leach-electrowin (RLE) route (Fig.- 3). Zinc sulfide mineral is first converted into zinc oxide, which is easily leached. The various steps in the process are described in more detail below.

**Roasting :** Zinc concentrate from various sources are blended to obtain an optimal mix of feedstock for the roasting process. During roasting, the zinc sulfides in the concentrates are converted into zinc oxide, known as calcine. A roasting furnace operates at a temperature of approximately 950° C generating enough energy to make the process autogenous. The roasting step also results in the production of sulfur dioxide-rich waste gases, which is converted into sulfuric acid in a contact process.

**Leaching :** The main purpose of the leaching process is to dissolve the zinc oxide contained in the roasted calcine material with sulfuric acid to transform it into zinc sulfate prior to the electrolysis stage. Approximately 90% of the zinc in roaster calcine is in the form of zinc oxide, with the balance being present as zinc ferrite, from which zinc dissolution requires more aggressive acid conditions. The leach residue goes for further refining for recovery of precious metals. The dissolved iron is removed from the zinc sulfate solution as goethite, jarosite, or haematite which is usually stored in ponds.

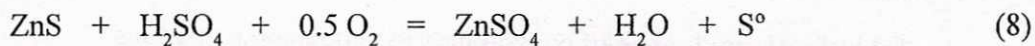


**Purification :** The leach solution is subsequently undergo purification to remove other dissolved impurities such as cadmium, copper, cobalt or nickel which could also affect the electrolysis operation. These impurities are removed through cementation by adding zinc dust to the solution.. The purified zinc sulfate solution is sent to the cell house for the electro-winning of zinc.

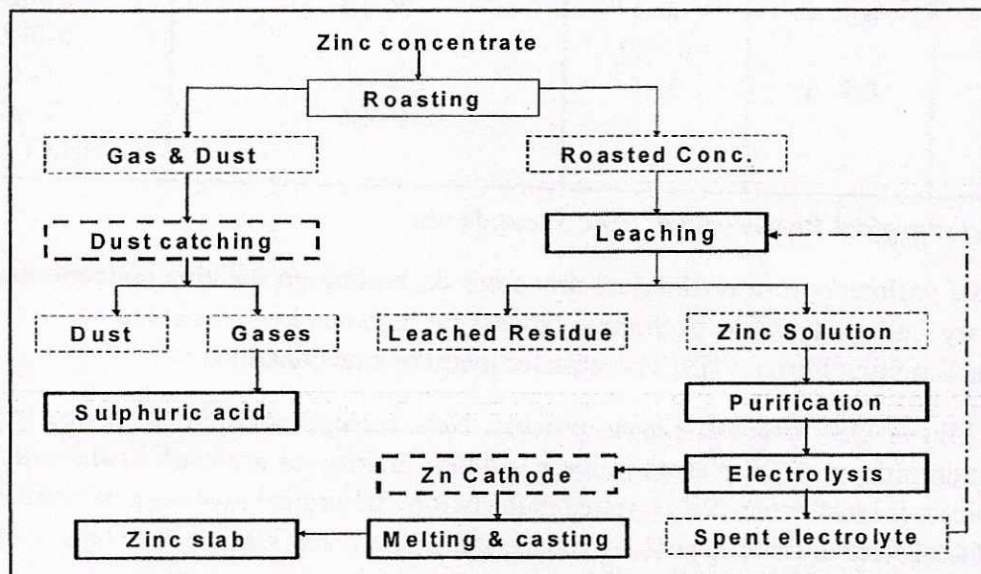
**Electrowinning :** Zinc metal is recovered from the purified solution by means of electrolysis. Zinc deposited on aluminium cathodes are removed at a regular interval. The zinc produced with the electrolysis process (SHG grade containing 99.995% zinc) undergo melting in an induction furnace and cast into marketable products.

**Pressure Leach Process :** The pressure leach technique was first successfully commercially applied for zinc extraction with the commissioning of first plant in 1981 at Cominco, Trail, Canada. There are presently three electrolytic zinc plants in the world where this technique has been integrated into the existing facilities. A fourth green field plant with two-stage counter-current pressure leach-electrowinning is under consideration.

In this process zinc sulfide or bulk zinc concentrates are oxidized under oxygen overpressures of 1200 kpa abs. at a temperature of 150°C in sulfuric acid medium to produce zinc sulfate solution directly and the sulfide content is precipitated as elemental sulfur according to the following overall reaction:



The various factors influencing the kinetics of above reaction are the particle size, mineralogy, surface active additives, acidities, reaction time, temperature and oxygen over-pressures where by maximising metal extraction and fixation of lead and iron constituents into disposable jarosite and other types of residues. The zinc sulfate solution thus produced is amenable to further processing for final zinc extraction through conventional leach-electrowinning process.



**Fig. 3 :** General flow-sheet for recovery of zinc from zinc concentrates by roasting-leaching-electrowinning process.

## 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.

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%

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	-	-	-	NH <sub>4</sub> Cl - 3.1

### 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.

Zinc dross is a metallic alloy of zinc and some iron which is generated during galvanizing operation is often processed by pyrometallurgical techniques. The commonly practiced methods for zinc dross processing are :

**Liquation and Remelting :** In this process the material is kept on a sloping hearth at a suitable temperature so that the molten zinc trickles down without effecting iron. However liquation is not suitable for the production of high purity zinc for galvanizing since the zinc that trickles down carries fine dross crystals and is oxidized in the process. The working temperature is high as a result zinc is contaminated with iron due to increased solubility. Recovery of zinc by this process is around 30% of the weight of dross treated. It has been reported that higher recovery of zinc from dross could be achieved by centrifuging and squeezing process.

**Aluminum Process :** Based on the aluminum addition Schmidt developed method for the recovery of zinc. Addition of aluminum leads to the displacement of zinc from crystals of zeta phases ( $\text{Fe-Zn}_{13}$ ) as the affinity of Al for Fe is greater than that for Zn. The alloy of iron and Al ( $\text{FeAl}_3$ ) requires only 1.5 parts of Al to 1 part of iron compared to the 15.5 parts of Zn in zeta phase. Density of  $\text{FeAl}_3$  is much lighter than molten zinc, hence it floats on the surface and its skimming is easier and efficient than scooping from the bottom of the bath. The operation is carried out at about  $720^\circ\text{C}$  and after the removal of skimming the metal is cooled and casted. Recovery of metal is around 85%.

**Electro Thermal Process :** This process of recovery of zinc has a number of advantages over the indirect distillation method such as:

- electricity is used as a source of heating making the process energy efficient
- recovery of zinc is 98% against 92% in distillation method
- removal of solid residue left after distillation is easier because as the crust can be remelted and tapped out by raising the temperature making the temperature continuous one.
- no retort or pot is required for holding the dross for distillation.

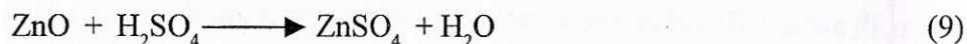
The process is feasible where the electricity is cheap. The capital investment is large and is feasible on large scale.

**Distillation Process :** In this process, zinc from dross is distilled off as zinc vapour from a retort and condensed in a suitable condenser. Three types of furnaces namely stationary, horizontal and tilting type are commonly used. The stationary and horizontal furnaces are similar in construction and size. These are made of firebricks and fired with gas or oil. The tilting type furnace consists of a large cylindrical steel casing lined with firebricks and mounted on trunions which facilitated tapping at an angle. In these furnaces, retort is used for melting the dross. The metal vapour/fumes from the retort passes into the condenser where it is cooled either as metal or as dust depending on the design of the condenser, alternatively the fumes/vapours from retort is allowed to burn in the adjoining combustion chamber in presence of air to form zinc oxide.

### ***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 sulfuric acid/spent electrolyte to get zinc sulfate 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 sulfate 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. 4. 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 sulfate manufacture. The fine ash containing mostly zinc oxide is treated with sulfuric acid to bring zinc values to sulfate form and filtered to get clear zinc sulfate solution. The solution is evaporated in a crystalliser and crystallised by cooling through chilled water to recover zinc as zinc sulfate.

**ZINCEX Process :** This hydrometallurgical process resembles conventional zinc electro winning and is readily integrated with such a plant. EAF dust is leached with sulfuric acid to solubilize zinc and cadmium oxide and halides. The impure zinc sulfate solution is treated by solvent extraction to remove zinc and cadmium and transfer them to purified, halide free, concentrated zinc sulfate solution. Cadmium is removed from the solution by cementation. High purity zinc metal is electrowon from the purified solution and sulfuric 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.

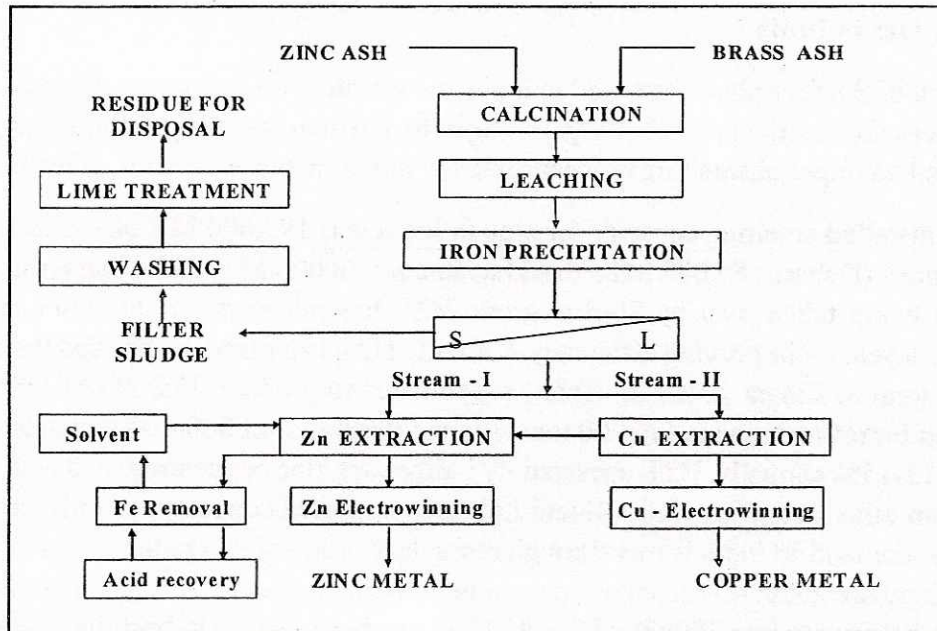


Fig. 4 : Solvent extraction and electrowinning process to treat copper rich zinc secondaries.

**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.

**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.

**WAELEZ 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.

**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.

## **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 Chittorgarh, 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. However, following Basel convention's 1989 decision where several developing countries including India put a complete ban on imports of hazardous and toxic wastes in to their territory. Among the items banned in India were lead and zinc ash and their skimming which has resulted in closure of most of the secondary units manufacturing zinc metal from scrap and wastes. But due to the pressure from various sectors and keeping view of the national interest few secondary units were provided licence for import and recycling of zinc secondaries.

## **CONCLUSIONS**

- Technology for lead & zinc production both from primary and secondary sources is well established.
- Most of the secondary zinc and lead manufacturers are adopting established and eco-friendly technology. However, care must be taken to control pollution by installing appropriate pollution control devices and adopt proper waste handling and disposal practices.
- Development and applicability of newer eco-friendly technology in Indian context must be initiated by the industries as well the national laboratories.