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PROBLEMS OF SECONDARY LEAD AND ZINC UTILIZATION[1]

by

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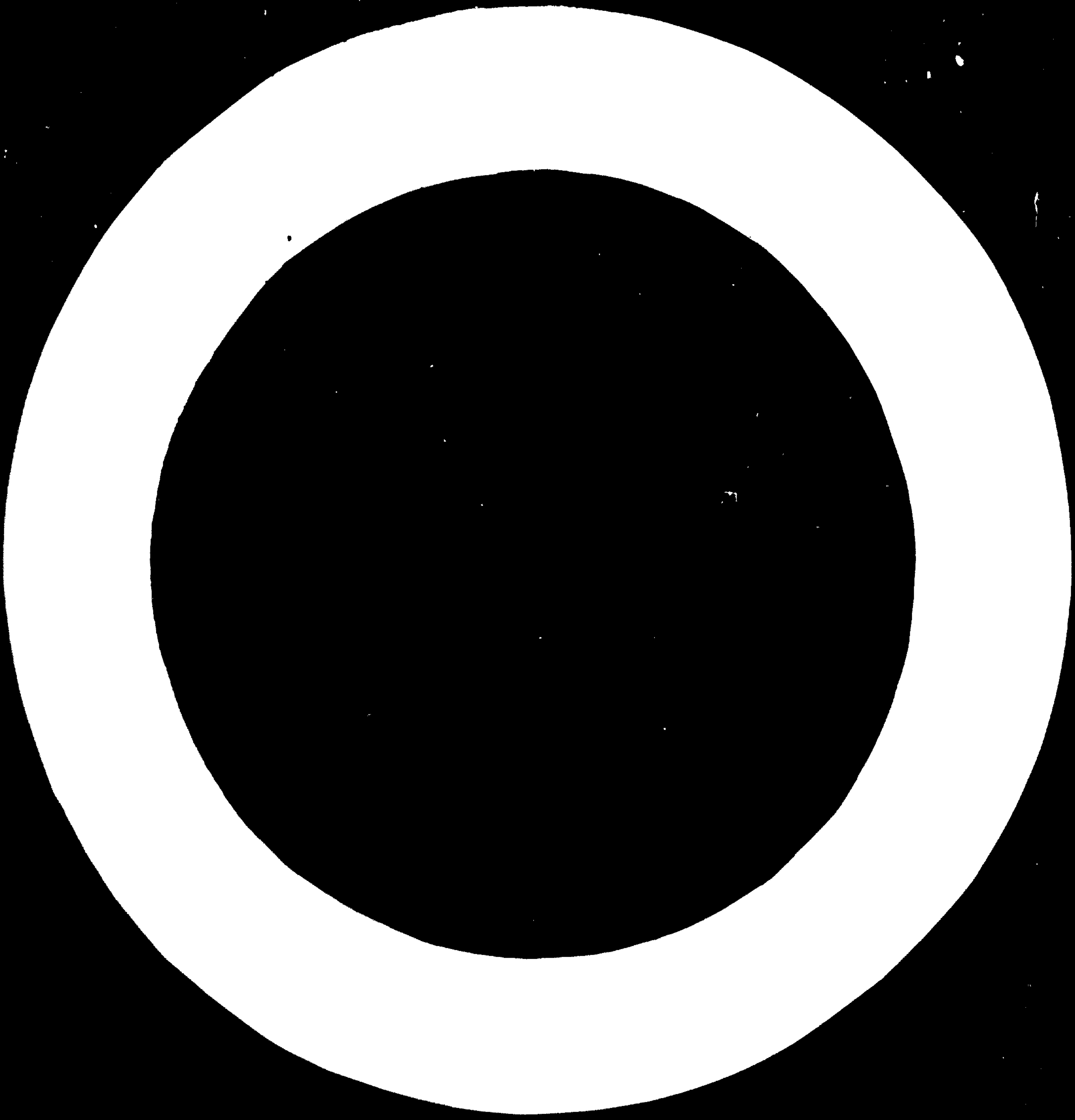

INTRODUCTION

Primary metals are derived from ores, while secondary metals are obtained by remelting, refining or smelting scrap and residues. In actual practice, however, no clear distinction seems to exist between the two categories since there are many variations and combinations of the two types of metal. Secondary metals play a vital role in the economy and today very little scrap and residues goes unutilised. Often, scrap, residues and other waste products are directly converted into other forms of the metal such as alloys or chemical compounds without going through the intermediate stages of recovery into secondary metals. Thus, secondary metals cover a much larger area than what is implied by the definition.

A time there was when secondary metals were considered inferior to primary metals. However, with the advancement of refining and analytical techniques, there is a better appreciation of the value of secondary metals. In fact, it is sometimes possible to produce a secondary metal of higher purity at a lower cost than the original virgin metal which gave rise to scrap or residues. Furthermore, with our more exact knowledge of the requirements of the purity of a metal or alloy for a certain application, it has been possible to achieve a more efficient and economic use of secondary metals. Thus except in a few restricted applications, secondary metals are extensively used on an equal footing with primary metals.

SOURCES OF SECONDARY LEAD AND ZINC

The sources of secondary lead and zinc are best discussed in the background of the various end uses of the two metals. Not all of the applications yield raw materials (scrap and residues) for secondary metals, since in a number of uses the metals are completely consumed during service. There is, however, a good availability of raw materials for secondary lead and zinc. The extent to which this occurs will depend on the total quantities consumed in a particular application and also to the proportion of scrap and residues arising out of this application.

Secondary sources for lead

The important and major uses of lead are : lead acid batteries, lead for cable sheathing, pigments, sheets and pipes in building and plumbing. Besides these major uses, lead is used in numerous other applications such as printing metals, bearing metals and lead tetraethyl, lead for sound insulation, etc. On a global basis, the most important application of lead is for batteries, followed by cables, sheets and pipes in building, pigments and anti-knock compounds. In addition, the numerous minor uses of lead approximately account for about 20% of the total lead used. Fig. 1 depicts schematically the various applications of lead that yield raw materials for secondary lead and their relative importance. Actual pattern of usage varies from country to country but the diagrammatic representation indicates the potential availability of secondary metals for the various applications.

Secondary sources for zinc

The most important uses of zinc are for galvanizing, die casting, brass, wrought zinc and pigments. Fig. 2 is a diagrammatic representation relating to the various applications of zinc and the availability of secondary metals. Here again, there are gross variations between individual countries but it may be noticed that significant quantities of the metal are available from the secondary metal industry.

RECOVERY OF SECONDARY LEAD

Lead from batteries

Lead from used batteries contributes more than 50 - 60% of the total secondary metal produced. Lead bearing materials in exhausted batteries consist of grids and pastes containing metallic lead, antimony, lead oxides and lead sulphate. Lead is usually recovered as an alloy of antimony either by processing the scrap alone or with other lead bearing residues. While the battery grids are made of antimonial lead, pure

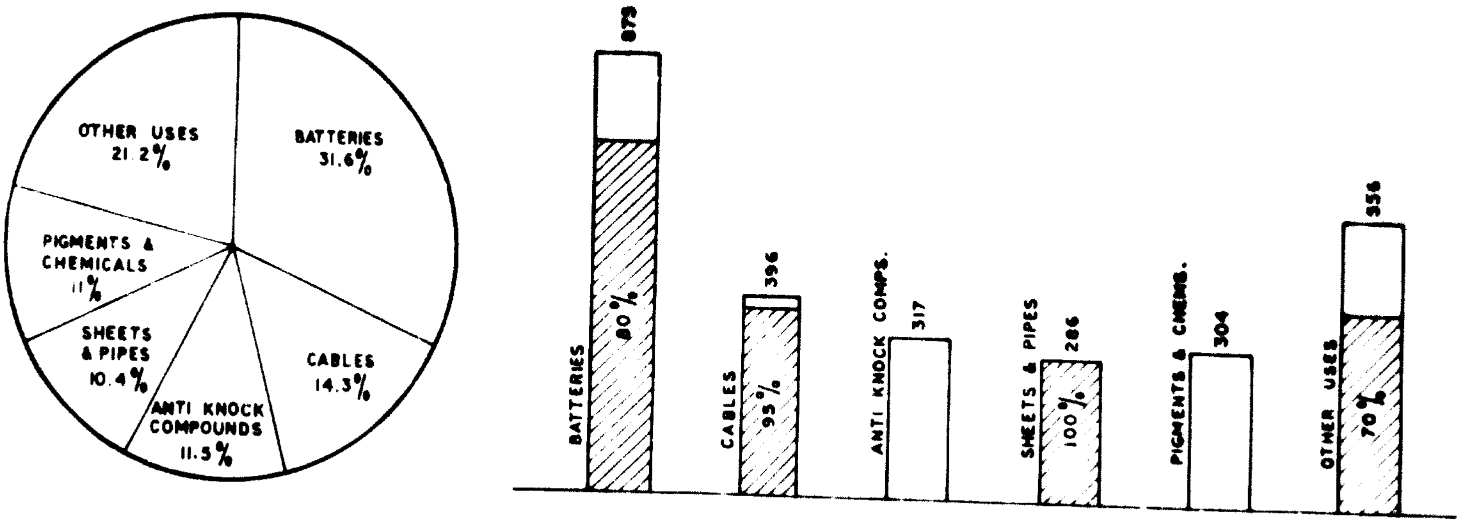

Fig. 1(a) End-use pattern of lead consumption (1967)

(b) Potential availability of secondary lead* from various applications

(Consumption figures are in thousand metric tons)

*The availability of lead scrap may be spread over a number of years, depending on the application. For example, batteries return to the scrap market in 2-3 years while cables, sheet and pipes may enter the scrap market after 20 - 50 years or so. This diagram merely indicates the potential lead that can be re-used. The shaded portions indicate the percentage of lead that would be ultimately available.

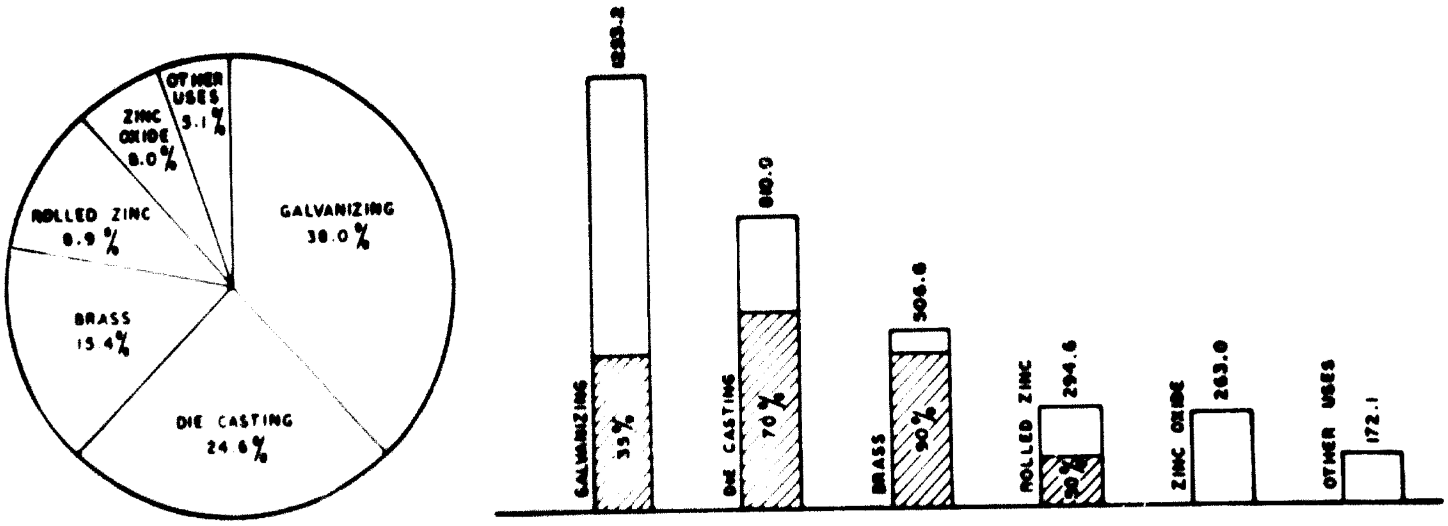

Fig. 2(a) End-use pattern of zinc consumption (1967)

(b) Potential availability of secondary zinc* from various applications.

(Consumption figures are in thousand metric tons)

*The availability of zinc scrap may be spread over a number of years, depending on the end-use. The shaded portions indicate the percentage of zinc that would be ultimately available.

lead is used in the manufacture of the active material. It is the usual practice to aim at the recovery of an antimonial lead alloy rather than pure lead, and the recovered alloy is used again in the battery industry after making up the antimony content. Battery scrap may be treated in simple melting pots, reverberatory furnaces, barrel furnaces, blast furnaces and less commonly in electric furnaces. Simple melting techniques cannot yield all the recoverable lead since the active material is in the form of oxide and other compounds and this calls for smelting. The principle is fairly simple and consists of treating the battery scrap with suitable reducing agents and fluxes. The latter help in the easy collection of all the metallic content and the reducing agent reduces the oxide to the metal. There is however a large variation in the practice, the technique and the different additives to the smelt.

Metal literature contains numerous references on the methods of recovery of secondary lead from battery scrap although in a good many of these, details of the process are somewhat scanty, particularly in regard to yield, efficiency, etc. A survey of literature indicates that although the recovery is being carried out all over the world successfully on a commercial basis, still the techniques followed in general are far from ideal and no systematic investigations have been carried out to establish the most efficient and economical method of recovery. Bigger plants which are assured of a consistent quality of scrap operate on better efficiencies and yields. Most of the smaller secondary metal producers usually follow their own methods based on trial and error rather than well established research work. Handicapped by inadequate technical facilities, their problems become even more complicated as a result of having to use non-uniform scrap and at times being forced to treat battery scrap with other lead bearing residues.

Old batteries are collected by scrap merchants directly from the customers or through battery dealers. These are then bought by secondary metal refiners or in certain cases by the battery manufacturers who have facilities for reclaiming the metal. The problem of retrieval of the metallic contents of the battery from the non-metallics, viz. containers, separators, etc. can pose difficult problems particularly when huge quantities are involved. If only small quantities are required to be treated, separation of the battery plates together with the active material can be achieved by removing the top of the battery with a gas torch and collecting the lead bearing material by manual methods. While this is possible where the quantity treated is small and labour is cheap, they cannot be applied in places where large tonnages of the metal are treated. This has led to the development of a number of patented automatic processes (1-4) by which the metallic contents of the battery are separated from the inactive material. All these methods utilize the difference in specific gravity between lead and other materials. The batteries are usually charged in a pulverizer where they are broken into small bits and fine powder. The material is then sifted by mechanical means or sieved wet or treated in a separation vessel containing a liquid medium of the proper specific gravity which helps in the separation of the heavy non-metallics from the light inactive material.

Thermal methods of lead recovery from battery scrap

Earlier work on smelting of lead scrap indicates that recoveries were very low mainly as a result of losses in fumes and slag matte, the latter resulting from the sulphur content of the scrap. In a study of these factors (5), the scrap was washed in a concentrated solution of soda ash whereby the sulphur content was almost completely eliminated. The washed scrap was then smelted in a reverberatory furnace employing a temperature of 800 - 900°C. The flux used was a mixture of soda ash, borax and flourspar with anthracite as a reducing agent. It is claimed that 98.5% of the lead and antimony contents were recovered and fume and metal losses in slag were negligible.

A patent (6) of a Japanese origin describes the treatment of a mixture of battery plates and antimony slimes. In this process old battery plates together with half their weight of antimony slimes (55% antimony) are heated at 700°C with 5% wood charcoal, 10% Na_2CO_3 and 10% coal tar. The yield was of the order of 92% containing an 18% antimony alloy. In a second Japanese patent (7), wastes of storage battery plates, etc. containing sulphur are moulded with carbide sludge and are subsequently smelted with a suitable reducing agent.

Yet another Japanese patent (8) claims a relatively high recovery of 93.5% of lead in a process using electric furnace without any pre-treatment for the elimination of sulphur. The scrap contains 82% antimonial lead, 3.5% sulphur and 4.5% moisture. The furnace is equipped with a bored graphite electrode through which SO_2 can escape rapidly.

A recovery of 87% is claimed (9) while treating battery scrap containing 80% lead and 2-3% antimony in a shaft furnace with a natural draft using 2.5% of the charge as a reducer. Better results (10) have been obtained using an electric shaft furnace with a charge containing tailings of lead and battery scrap.

In another method (11) scrap is treated with a 1 : 1 mixture of sulphur compound of sodium and sodium hydroxide at a temperature of 360°C ± 20°C, stirring the mixture with a mechanical device. The particular advantages of this process are the relatively low temperature, high purity of the reclaimed metal, absence of fumes, low lead losses and no necessity for any special apparatus.

While some of the patents claim very high recoveries, commercial practice in Britain (12) adopting rotary furnaces claims about 75% recovery in the case of car batteries and 90% in the case of large storage batteries. The charge is usually made up of battery plates with 2% sodium carbonate, 2% coke, charcoal or anthracite, ½% sodium chloride and ½% cast iron filings. The temperature is 850°C. The relatively low yield is due to the loss of some metal in fumes which if collected in bag houses and resmelted can result in higher metal recoveries.

In a paper (13) reported from Holland, battery-scrap lead containing about 20% by weight lead oxides is charged in a rotary drum melting reduction furnace and treated with solid carbon (10% by weight of lead charge) and 10% Na_2CO_3 which functions as a drossing agent. The dross-free molten lead is pumped into a refining furnace and treated with sulphur to remove copper. After the removal of copper dross, the metal is treated with a mixture of NaOH and $NaNO_3$ to refine it further.

Extensive investigations (14) on treatment of battery scrap and the residues of lead were carried out at Kurilo, Bulgaria. Various methods and furnaces such as blast furnaces (industrial as well as experimental), rotating barrel furnaces and electric resistance furnaces were used. Investigations included treatment of selected battery scrap as well as scrap with other lead bearing materials. The investigations revealed that separate treatment of lead battery scrap was more efficient than a combined treatment of battery scrap with other lead bearing materials. Electric resistance furnaces were more efficient and gave higher yield of metal of greater purity.

An East German (15) patent describes a process in which metal fractions of low sulphur content and fractions containing sulphur are treated separately. The former are treated in fusion kettles while the products containing sulphur are treated to give basic lead sulphate in liquid form. This compound is then reduced to metallic lead.

Electrolytic methods of recovery for battery scrap

While thermal methods of recovery are widely used all over the world, there have been some attempts to reclaim the metal by electrolytic methods. These are mostly restricted to laboratory investigations or pilot plant studies. Data relating to capital or working costs are lacking.

Two different methods (16) of recovering lead from active materials of old lead acid batteries have been developed by the Central Electrochemical Research Institute, Karaikudi, India. In one of them, a 50% alkali solution is employed as an electrolyte and the active material is kept in suspension. The cathode is a stainless steel and the anode is made up of mild steel. Lead is obtained in a spongy state. In the other method, the active material is soaked in 20% alkali to form a depolariser in contact with cathode. A layer of electrolyte on the settled solid forms the anode. Conditions have been determined for reduction of the oxides to the metal. These two methods are also applicable to scraps and other residues of lead (17). The same Institute has also developed a method of obtaining pure lead from an alloy of lead and antimony using a fluoborate bath (18,19). By using an alkali of 25% strength lead is obtained in a powder form (20,21). In a process using molten NaOH as electrolyte and iron electrodes (22), electrolytic reduction of oxides of lead is achieved without much consumption of the electrolyte.

Lead from cable sheathing

Lead for cable sheathing is a very important application next only to batteries and appreciable quantities of scrap are available although somewhat in a sporadic manner in contrast to battery scrap whose supply is very uniform. The battery after usage is certain to return to the scrap market in 2-3 years whereas there is no such regularity in respect of lead from old cables.

A certain amount of scrap is available within the factory and these include lead which is extruded while press adjustments are made, and sheaths of factory rejected cables. These are very good scrap and are simply returned to the melting pot for reuse. A small quantity of residues in the form of dross, skimmings and droppings from leaky valves is also available but these are usually sold to scrap markets which process them along with other lead bearing residues. When lead is used as a temporary sheath for vulcanising rubber insulated cables, it can be stripped and remelted without encountering any problems provided a ram press is used. If, however, a continuous screw machine is used, lead tends to get contaminated with oxides and sulphides and has to be cleaned before use. This also is usually done within the cable works itself by sodium treatment but sometimes it is sent out for processing (23).

Sheathing from old cables is almost always treated by secondary metal refiners. Most of the cable strippings are old lead and require making up to the correct alloy specification before they can be used. Refining treatment will depend on the impurities and the subsequent use to which the lead will be put.

Lead from sheet and pipes and other miscellaneous uses

This is a major source of secondary lead in some of the developed countries and the scrap market receives a steady and uniform supply of scrap. In the developing countries, scrap arising from this source is relatively small as the take off for this application is insignificant. The scrap obtained from this source is invariably contaminated and so inhomogenous that no selective treatment is tried but it is usually given a comprehensive refining treatment (24) to remove all the commonly known impurities such as Cu, Fe, As, Sb, Sn, etc. Scrap is melted in large cast iron basins which are provided with mechanical stirring arrangements. After the charge is molten, the dross rises to the surface and is skimmed off. The dross is treated separately and the molten metal is transferred to a refining kettle where copper and iron are removed by the action of sulphur and ammonium chloride. Other impurities such as arsenic, tin and antimony are removed by the action of a flux based on NaOH. There is some loss of metal in the form of fumes which can be collected and reclaimed. This, however, is not done except in fairly large secondary metal refineries.

In addition to the above process which is widely used for the recovery of lead, there are other patents relating to special types of scrap in the form of powder, filings, borings and other miscellaneous scrap and those containing other less common impurities. An Italian patent (25) entails acid washing of the scrap and/or addition of a suitable flux like NH_4Cl, H_3BO_3, HCl and $HClO_4$ prior to melting and fusion. The process is claimed to give a good recovery. A French process (26) used for treating high-bismuth lead is based on the formation of the ternary compound $Bi_7Mg_6K_6$ by the addition of magnesium and potassium to the crude bismuth-lead. In a process developed in Czechoslovakia (27), a copper-base waste material was given a chlorination treatment for lead removal. Lead can be recovered up to the last 2-3% within 15 to 25 minutes. Electrolytic methods (28, 29) are also available for recovery of lead from contaminated scrap. Aqueous solutions (28) and fused salts (29) are used as electrolytes and in a process using the latter, it is claimed to remove a host of impurities like Bi, Sb, Cu, Ag, etc.

Type metals

Printing metals have lead as their major constituent. The printers themselves melt and cast the metal a number of times during the course of their day-to-day working. Each melting leads to the progressive depletion of the alloying elements. When the metal has been used in a number of cycles, it is sent to a secondary metal refiner for 'reviving' the alloy. The refiners replace the spent alloy with an alloy of correct composition and usually accumulate the depleted alloys. When sufficient quantities are available, they are melted and after determining the deficiencies, they are restored to the correct composition by suitable alloy additions.

Dross and slag

During the various operations connected with the refining and production of lead, an appreciable quantity of dross (even as high as 25%) is produced. Therefore, several attempts have been made to treat this dross for lead recovery. Lead of 93 - 97% purity was obtained by treating dross with NaOH in a reverberatory furnace (30). Industrial drosses have been successfully treated (31) with sodium carbonate and calcium fluoride in rotary drum furnaces obtaining a recovery of 65% of lead. In a Canadian process (32) hot slag is treated with powdered coal and air and the reduced metals are vapourised and oxidised. This method claims the recovery of almost all zinc and major portion of lead from blast furnace slag. A Japanese patent (33) describes a process in which slag containing PbO is treated with B_2O_3, Na_2CO_3 and NaCl at 200 - 300°C and lead separates out at the bottom. If lead in slag is present as sulphate (34) it can be recovered by measured additions of $CaCO_3$ and Na_2CO_3 and fusion of the charge with sufficient carbon. Another method (35) reports the recovery of lead from the PbO of slag by a fusion treatment with $CaSO_4$ and Na_2SO_4.

A two stage process developed in U.S.S.R. (36) involves the treatment of slag and other semi-finished products in an electric furnace. In the first stage, copper and noble metals are extracted into a matte, while zinc, cadmium, lead and the rare metals are volatilized. In the second stage, the remaining lead and zinc are extracted. In another process (37) zinc slag containing zinc, lead and copper is treated in an electric furnace using coke as the conductor between the electrodes. A recovery of 85-96% of lead is claimed. Lead was separated from fused slag by cementation with carbon-saturated liquid cast iron. Lead recovery varied between 77 and 96% (38). Electrolytic treatment of slag at elevated temperatures has yielded good results (39). Separation of lead by leaching (40) with an alkali solution has also been successfully effected. The leachant converts arsenic, tin and antimony to their respective sodium salts, while the residue is treated for lead recovery.

Lead from slimes, tailings, fumes and dusts

Secondary lead in fairly significant quantities can be obtained from metallurgical wastes such as slimes, tailings, fumes, dusts, etc. Lead contents in these residues vary widely and they are usually admixed with a number of impurities which are difficult to remove. Furthermore, collection of some of the residues like fume and dust may be difficult. Even though they may contain a good amount of lead, economic recovery of the metal may not be possible since the collection of the residues needs expensive and sophisticated equipment. Nevertheless, these are important sources of secondary lead and are worth considering at least during emergencies and when there is acute shortage of the metal. This is borne out by the fact that there are numerous patents and processes for the reclamation of lead from the above residues. They include thermal (41-49), hydrometallurgical (47, 50-55) and electrolytic methods (43, 56-59) of recovery.

RECOVERY OF SECONDARY ZINC

The sources of raw materials for secondary zinc, either for the extraction of pure metal or for conversion to alloys and compounds will be discussed in the background of the end uses and applications of the metal.

Zinc from galvanizing residues

Galvanizing is by far the most important application of zinc. The residues formed during the galvanizing process are dross, ash, flux skimmings and steam blowings from the tube industry and these are important sources of secondary zinc. The total percentage of residues may vary from anywhere between 20 and 50% of the total zinc consumed. Among the residues obtained during the process of galvanizing, zinc dross is the most important raw material for secondary zinc since it contains the highest percentage of zinc and is easily amenable to extraction of the metal or utilization in other products of zinc. Ash is the next important residue and is a popular raw material for the manufacture of zinc compounds. Even flux skimmings do not go unutilised although they are more difficult to process.

Zinc from dross

The percentage of dross formed during the galvanizing process varies over wide ranges (5 - 40% of total zinc consumed) depending on the ware galvanized and other operating factors (60). Dross contains as much as 95% zinc and is thus a very rich source for extraction of the metal. It is also utilized directly to manufacture zinc dust and compounds of zinc and sometimes alloys. The various methods of extraction of zinc and utilization of dross will be discussed in brief below :

The important uses to which dross is put in most countries are (61) :

1) as raw material for the production of zinc dust
2) for the production of zinc oxide, and
3) reclaiming zinc in the form of secondary zinc.

The actual pattern of the usage of dross differs from country to country depending on the demand for various end products. In a number of industrially advanced countries like the U.S.A. and most of the countries in Europe, bulk of the dross is taken up by the zinc dust manufacturers. Dross is a very good starting material for the production of zinc dust and the principle here consists of melting dross and distilling the zinc vapour which is condensed in a large vessel where it solidifies in the form of fine dust. The principle of the process is very simple and it also does not need expensive or sophisticated equipment. Nevertheless, the process needs good control and standardization to produce fine powdered zinc of consistent quality as required in the various specifications.

Although in some countries zinc dross is used for the production of zinc oxide, it is not a popular raw material, since firstly other cheaper residues like zinc ash are available and secondly the zinc oxide from dross is somewhat tinted due to the presence of impurities and thus not acceptable to the paint industry as a first class product.

Distillation technique

Dross is a very good source for recovering pure zinc and in view of the low boiling point of the metal and other alloying characteristics of zinc, it lends itself to easy and relatively inexpensive methods of recovery.

Of all the known methods of recovery of zinc from dross, the distillation process (62-66) is the most suitable and has found wide commercial acceptance since this permits reclamation of free as well as the alloyed zinc. The method is based on the simple principle that when dross is heated at a temperature above the volatilization of zinc, the vapours escape and these are collected as liquid metal in a condenser. Almost all the impurities are left behind and relatively very pure zinc with recoveries up to 95% has been obtained. Most of the distillation units are small consisting of an oil or gas-fired retort and condenser. However, large size distillation units which are continuously operated are also in use (67,68). Distillation techniques employing electric resistance heating (69 - 71) and high frequency heating (72) are in operation and yield in the latter is reported to be of the order of 95%. Vacuum distillation techniques (73-75) have the advantage of employing lower temperatures, but in general they have not gained wide acceptance because of higher capital costs.

Aluminium process

Another process of recovery of zinc which is not widely used is based on the principle that aluminium has greater affinity for iron than zinc and thus can displace zinc from the zinc iron alloy (76-79). Calculated quantities of aluminium are added to molten dross and the iron forms compounds with aluminium and floats on the surface of the molten zinc. Although the process seems to be simple, in actual practice a clean separation is not possible and therefore the process was modified (80-83) to a certain extent by an intermediate treatment with lead to achieve greater ease and quicker output. The process is claimed to give good yield particularly when run continuously and the lead is re-cycled for subsequent operation. Furthermore, the advantages are that the equipment required is fairly simple and ordinary mild steel can be used as reaction pots. The U.S. Bureau of Mines had developed a novel method (84) of recovering zinc from dross by centrifuging and this is used alongside the aluminium process and the dross mixed with aluminium is subjected to centrifugal action when the liquid zinc is separated leaving a residue of solid iron aluminium alloy.

Other processes for dross

In addition to the well established methods of reclaiming dross, there are other simpler ways of recovering the metal. These consist of sweating out the zinc by a process of liquation (85, 86) or heating the dross and decanting the supernatant liquid metal (83, 87). In all these methods yields are poor and the metal is almost always contaminated with iron.

Zinc from galvanizers' ash

Galvanizers ash is an equally important residue which serves as a raw material for the recovery of zinc as well as its conversion to important zinc compounds. Ash may constitute anywhere between 10 - 40% of the total zinc used in the process depending on various operating factors. The total zinc content in the ash may vary between 70 - 90%, the other impurities being lead, iron, chlorides etc. Ash contains quite a good percentage (average 60 - 75%) of free zinc which gets entrapped when ash is removed from the zinc bath. It is normal practice in the galvanizing works itself to separate the coarser fractions from the finer. The former is usually charged back in the galvanizing pot or alternatively separately melted with a flux and the metal so obtained used again. This, however, may not be more than 5 - 10% of the total ash since predominantly ash is very fine. There are several methods to recover zinc from ash some of which are simple and can be practised at the works itself while others require considerable capital investment and could be handled only by secondary metal producers. The most common method used at the galvanizing works is the cylinder method which is nothing but an open-ended straight (87) or conical cylinder (88) kept at one corner of the bath partially immersed. Ash is fed into the cylinder and occasionally stirred. The heat from the bath melts the metal in the ash and the stirring allows the zinc from the ash to run back into the bath. It is claimed that 80 - 90% of the metallic zinc in the ash can be recovered (87). A British patent (89) claims that zinc in the ash can be reclaimed simply by providing a molten layer of one or more fluorides or chlorides of alkali metals on a portion of the bath.

In spite of the advantages of the cylinder method, very few galvanizing works adopt this as a routine practice because it takes up a portion of the galvanizing bath. Therefore ash is mostly treated separately and in general this is sold to secondary metal producers. The static crucible method (90) consists of treatment of ash with a suitable chloride flux in an externally heated crucible which is started first with a heel of molten zinc. Ash is initially given a gentle crushing to break lumps and is charged into the crucible and stirred well and the temperature is kept between 450 and 500°C. The principle of recovery is simple in that the exterior oxide surface is broken and the molten zinc is allowed to coalesce. Recovery of even 80% has been claimed. The rotary furnace (78, 87) is more expensive and consists of a bottle-shaped rotating crucible fired by gas or oil. There are other types of furnaces (91 - 93) such as the reverberatory furnace but these do not seem to be particularly advantageous either from the point of view of consumption of fuel or yields.

After the metallic portion of the zinc is recovered, the spent ash which is predominantly made up of zinc oxide is usually sold to chemical industries for the manufacture of compounds such as zinc chloride and fluxes but it can be smelted to recover zinc (94). In another method (95), it is mixed with zinc concentrates, roasted together and the roasted mixture is then distilled. But by and large in many countries the ash is bought by the zinc oxide manufacturers who use this as a raw material for the production of zinc oxide by the direct process (96). An Indian patent (97) describes a method in which the material is heated in a tumbling barrel which contains sodium carbonate and caustic soda solution. After the neutralization of chlorine salts, the resultant oxide is washed and dried and used for the production of zinc carbonate by passing CO_2 gas through a rotating heated cylinder containing ash and water. Roasted zinc ash is also used in the manufacture of lithopone by leaching the ash with sulphuric acid and the purified zinc sulphate solution forms the raw material for producing lithopone. A number of galvanizers use the ash to produce zinc chloride by dissolving the ash in hydrochloric acid and after adequate cleaning, it can be used as a flux.

Zinc from flux skimmings

Flux skimmings are residues obtained in the wet galvanizing process and are composed of zinc oxides, zinc chlorides and other chloride impurities with some metallic zinc. This is not as good a residue as ash or dross and is mostly purchased by the chemical manufacturers who buy them at a much lower price than ash or dross. A process developed in the U.S.(98) claims that all zinc values present in the flux skimmings can be recovered as a high purity metal. In this process, the skimmings are reacted with calcium oxide or burnt lime when the chloride of zinc and other metals are converted into oxide and calcium chloride is obtained as a by-product. After treatment in a ball mill with petroleum coke and burnt pebble, it is heated in a graphite crucible containing molten $CaCl_2$. Zinc oxide is reduced and the metal collected in a condenser. Another U.S. patent (99) describes reclamation of zinc from skimmings which begins with a grinding operation of skimmings immersed in an aqueous solution of sodium carbonate. The chloride contents are removed by filtration while the residue containing zinc is treated in a conventional retort using coke as a reducing agent. An Indian patent (97) describes the method by which first skimmings are made free of chlorides by treatment with an alkaline solution. The residue is mixed with charcoal, tar or slaked lime and reduced in a rotary furnace and the metallic zinc that is formed is reoxidised and the oxide collected.

Steam blowings

There is another residue from the galvanizing industry particularly from the tube sector. When tubes are galvanized, the excess of zinc on the inner surface is removed by steam blowing and during this process some coarse as well as fine particles of dust are driven off which are collected in dust collectors. This residue may form approximately 10% of the total zinc used for galvanizing. The coarser portions of zinc are relatively pure and are usually fed back into the bath itself. The finer portions of zinc are consumed by chemical manufacturers. The very fine portion consisting predominantly of dust is also taken by chemical manufacturers since in spite of its fine size, it cannot be used for paint manufacture because of high oxide contents.

Die casting scrap

The next important application of zinc is in die casting. There are two types of scrap here - one that is produced during the die casting process in the form of runners, risers, gates, rejects, etc. and the other old and useless die castings. The former is used in the die casting plant itself where it is mixed with virgin metal for the manufacture of alloys. The second type of scrap, viz. old die castings which are obtained from unknown origins is more difficult to deal with. Normally, it would not be advisable to use it for die casting unless complete analysis of the whole lot is made. Such scrap may be used for the recovery of zinc by distillation methods or for the manufacture of zinc oxide. A limited use of this alloy can be made also in galvanizing where it may be used as an additive for brightening galvanized ware (100).

Zinc sheets

Zinc sheets form the next important use of zinc. Scrap obtained from roofing can be remelted and depending upon its purity, can be used in many applications as secondary zinc either in galvanizing or brass making. But sheet zinc is going out of usage in many parts of the world with the introduction of galvanized steel and therefore zinc sheets for flashlight batteries appear to be the most important application of this material. In this application, the sheet functions as a container as well as an electrode and a good portion of the zinc sheet remains intact even when the cell is no longer in use. Bulk of the zinc from the cell can be recovered and re-used. However, the collection of spent cells and subsequent separation of the zinc sheets from the content of the flashlight battery is such a laborious operation that these cells by and large find their way to the garbage heap. Further research work is needed in the collection and separation of zinc from cells. Zinc from spent batteries, even when separated, are very thin and it would be advantageous to briquette them and then remelt so that loss can be reduced to the minimum.

Other residues

There are other types of residues obtained in the chemical industry as for example the sludge in the hydrosulphite industry. In some countries, this is consumed by chemical manufacturers whereas in India two processes have been recently developed, one of which is a thermal method (101) by which the sludge is mixed with carbonaceous material and charged into an electrically heated retort furnace where zinc is allowed to volatilize and condense in the form of fine dust. The Central Electrochemical Research Institute has developed another method (102) for converting sludge back into zinc dust by an electrolytic process. Both these processes have been perfected and are ready for commercial exploitation.

Zinc from brass scrap is seldom recovered and mostly they are remelted and made up by addition of zinc or copper and reconverted into secondary brass.

While the above covers the reclamation from the more important sources of secondary zinc, a significant quantity of zinc is available from slimes, dusts, drosses, ashes, sludges, etc. which arise out of various processes such as blast furnaces, various smelting and alloying operations. These residues vary very widely in composition so that each of them may require special methods. There are numerous patents and processes available and these include thermal, wet and other hydrometallurgical operations and electrolytic methods. In some cases, because of the complex nature of residues, more than one process have to be adopted. It will not be practicable to even discuss the gist of the methods, references to which are available in literature (103).

ECONOMIC ASPECTS OF RECOVERY OF LEAD AND ZINC FROM SCRAP AND RESIDUES

The economic aspects of the recovery of secondary lead and zinc are not in any way significantly different from those governing other metals. However, there are some special factors concerning the two metals, a discussion of which will lead to a better appreciation of the utilization of secondary lead and zinc from scrap and residues.

Collection of scrap

Problems relating to the collection of scrap and residues have an important bearing on the economics of secondary metal recovery. In this context, two applications of the metals which represent extremes from the point of view of the ease with which the raw material can be collected will be considered. Take, for instance, flashlight batteries which is a fast growing zinc consuming industry, particularly in the developing countries. In this application, a significant portion of the zinc which serves as the container and the electrode remains intact even after the battery is exhausted. Thus it should be a very good source for secondary zinc if only all the old batteries can be collected and the zinc recovered from them. However, collection of spent batteries is no easy task since the batteries are very widely distributed throughout the country. At times of acute shortage of the metal, there have been sporadic and indifferent attempts to collect the spent batteries. Efforts to collect old cells through retail dealers by requiring consumers to turn in old cells for new ones have largely been unsuccessful. As against this example, collection of lead acid batteries is relatively easy and the scrap collection is a fairly well organized commercial sector so that almost all old batteries eventually reach the secondary metal refineries which are assured of a smooth and steady supply of the raw material. In this case, conditions for collection are very favourable as the user has an incentive to turn in the old batteries to the scrap merchant or dealer because of the price for the old battery or the discount on the new one. There is adequate metal in each unit of a lead battery that trading of the old battery for scrap is profitable. Furthermore, the bulky size of the lead battery facilitates easy collection whereas the small flashlight battery with insignificant metal content usually is disposed of in the dump.

There is another application, viz. die casting, from which there should be a large potential arising of scrap. However, because of the difficulties of collection, a portion of the metal is lost since die casting scrap is usually mixed with other assorted metallic scrap and it is extremely difficult to segregate it for recovery of zinc.

There are other sources of raw materials for secondary metals which do not pose any difficulties in respect of collection. For instance, dross and ash form significant portions of the zinc consumed in galvanizing which is the most important application of the metal. The difference between this and the earlier application is that the raw material for secondary zinc does not get diffusely distributed and is available with the manufacturer himself. Another important difference is that the galvanizer gets paid for the residues or he profitably reclaims the metal himself. Others, for instance the lead acid battery manufacturers, have to pay for the scrap and a portion of the cost of the scrap is accounted for by the charges for collection through various intermediaries.

Retrieval of the metallic contents and cost of recovery of metal

In addition to the collection of scrap, there are two important factors concerning the economic recovery of secondary metals. One of them relates to the retrieval and segregation of the metal bearing portions from other ingredients and the second deals with the cost of recovery of the metal from scrap or residues.

Often, the metallic portion of the scrap is not readily available in a form where it can be processed by simple refining or smelting. A good clean scrap for example is the loose scrap from old buildings and plumbing fixtures which therefore fetches a good price. Most of these can be used after a simple refining treatment. In a lead battery on the other hand, the lead bearing paste and lead-antimony grids have to be separated from the organic or other material (container, separator, etc.) and this is an intermediate operation which tends to raise the cost of the secondary metal. As already pointed out, where large quantities are involved, this operation is not simple and requires expensive equipment. There are other scraps and residues like metallic turnings from machine shops, assorted drosses, slimes, slags, dusts, etc. from various sources which are invariably complex mixtures of several metals and other extraneous materials. Such a raw material requires complicated preliminary treatment to separate the respective metals before further refining or smelting. These operations may involve sometimes a combination of wet, hydro and thermal techniques which naturally increase the cost of the secondary metal. It may at times happen that the cost of these treatments alone may be the sole deciding factor whether or not a particular residue is worth processing. While these kinds of raw materials are by themselves difficult to process, a further complicating factor is that they often vary in composition and other characteristics that would call for frequent changes in the pre-treatment process and thus render recovery of the metal to be impracticable. Another example worth considering is the recovery of zinc from flashlight batteries. Even assuming that all spent batteries can be easily collected, separation of the metal from the chemical contents will not be a simple process. No techniques seem to have been developed to separate zinc from the other materials of flashlight cells, particularly when large quantities are involved.

The cost of conversion of scrap and residues into secondary metals or other forms of acceptable products is another important factor deciding the cost of the secondary metal or product as also the price of the scrap or residue. A notable example is the lead acid battery which predominantly uses secondary lead in endless cycles. This is because secondary lead is available at a relatively lower price which is again due to the fact that refining and smelting techniques are not costly so that a cheap secondary metal is available in spite of the cost of collection and pretreatment. The galvanizers on the other hand seldom attempt to reclaim the residues for metallic zinc even though the secondary zinc would be acceptable in terms of quality. Here there are no problems of collection and preliminary treatment but still they sell it outside because firstly the quantity of arisings of residues is in general small and more importantly a number of other industries such as dust and oxide manufacturers are prepared to pay a good price for the residues. Thus the galvanizers are content in merely disposing it off to these industries. By and large, the tendency seems to be to adopt simple and inexpensive techniques to obtain the metal or alloy or a compound. Often it will not be economic to attempt the extraction of a high purity metal.

End product and primary vs. secondary metals

There are some processes which cannot use secondary metal at all, as for example for zinc die casting and possibly for flashlight batteries, photo engraving plates, etc. These industries require raw materials of a very high purity and rigid specifications so that it will be uneconomic for the secondary metal reclaimers to supply a product suitable to them. Considerable quantity of scrap is available from these applications, but it cannot be cycled back to the respective industries and has to find use elsewhere. The die casting industry can use some of the scrap arisings produced within the factory but it will not be able to use the scrap obtained from old die castings collected through scrap dealers. The relatively high aluminium content of the alloy and its nickel and chromium contents in the plating restrict the use of the metal and the scrap may at most be used for products such as zinc oxide and/or secondary distilled zinc. If these are the end products for which the scrap can be used, die casting scrap will have to compete with other residues like dross and ash which are also equally suitable for the purpose and these factors decide the price of scrap. Often die casting scrap has been used to produce an aluminium zinc alloy which can be utilized as an additive in galvanizing baths and thus could get a higher price for the scrap. It may be noticed that only in those applications which permit the endless use of secondary metals, the scrap and secondary metal market is well established.

Stability of prices of raw materials

In general, the price of scrap and residues follows sensitively the price of virgin metal, thus maintaining a stable balance between the primary and secondary metals, regardless of fluctuations and scarcity in the market. Without this it will be difficult for the secondary metal market to have stability. A good example is India where a stable secondary metal industry is not established mainly because of rapid and erratic fluctuations in the price of raw materials as well as virgin zinc. In India zinc is an imported commodity and allotted only to some priority industries.

Because of the scarcity of the metal in the country, often it turns out that the price of some of the residues (e.g. zinc dross) is in excess of the price of the imported virgin zinc. Naturally, the price of zinc in the open market is always considerably higher than that of dross or the imported metal. The primary reason for the high price of dross is due to the acute scarcity of zinc in the brass industry which often uses dross for purposes of alloying along with pure zinc and are prepared to pay a very high price for it since they can get a proportionately high price for brass. At that price, it is not worthwhile to attempt the recovery of secondary zinc. Furthermore, the deciding factor in these instances is the price difference between dross and open market price of zinc which alone will decide whether or not it would be economic to attempt recovery of the secondary metal.

Other factors

There are other economic aspects such as freight charges which sometimes play an important role in the utilization of lead and zinc scrap. In smaller countries, these may not pose very complicated problems but in large countries like India they might give rise to difficult situations particularly when it so happens that scrap has to be transported over large distances for secondary metal processing. It may also happen that the scrap producing industry may be situated far away from secondary metal using industries. These freight and other factors regulate the price of raw materials to a great extent and also determine how they will be utilised. For instance, because of freight costs alone it may be profitable for a plant to set up its own refinery rather than sending it out to a secondary metal merchant.

PROBLEMS PECULIAR TO THE DEVELOPING NATIONS

For the purpose of discussion, in this paper the following countries are mentioned as developing nations firstly because the industrial development in these countries is still at a relatively low level and their per capita consumption of metals, particularly lead and zinc, is very low. The developing nations form the southern part of the world comprising Latin America, Africa, Middle East, India and South East Asia (excluding Japan). They cover half the world's land mass and contain more than half the world's population. Almost all these countries are undergoing a big industrial expansion and the rate of consumption of zinc and lead in fact is increasing at a faster rate than the average world figures. From a mere 225,000 tons of zinc in 1961, it is expected that the consumption by developing nations would reach 700,000 tons by 1975. The corresponding figures for lead are 180,000 tons and 500,000 tons (104).

Scrap availability and scope for secondary metals

There are significant differences between highly industrialised countries and developing areas with regard to problems of secondary lead and zinc. The pattern of consumption of the two metals in developing nations is vastly different from the more developed countries, and it also varies from country to country. The picture is changing rapidly following the increased pace of industrialization. It is not unlikely that in a decade or so the pattern of use of the two metals in the developing countries will more or less fall in line with the rest of the world.

Taking lead in the first instance, battery appears to be the most important use with minor exceptions like Mexico where more than 50% of lead is consumed by the pigment industry (104). In a number of developing countries the battery industries are merely assembly units using imported grids and other parts, while in certain countries like India and Ceylon, the complete unit is manufactured. The former naturally have no use for scrap at present, while the latter are keenly interested in the utilisation of scrap and in fact a portion of the lead used is from reclaimed scrap. However, the percentage of scrap used in the manufacture of batteries is very much below that in highly developed countries. This is partly because the scrap industry is not well organized and there are not adequate facilities for refining and reclaiming scrap. Occasionally there is a lack of appreciation of the cost savings involved in the use of secondary lead and this has led to a slower pace in the adoption of predominantly scrap as the raw material for the battery grids. Furthermore, scrap arisings are not sufficient and supplies are irregular so that the installation of secondary lead refining units would not be economical. This is further aggravated by a chronic shortage of the metal as a result of which the battery scrap gets diverted to other applications for which primary metal may not be readily available.

Except for India, most of the other countries do not have any big cable works and the cable consumption is insignificant and there is very little scrap arising out of this application. Most of the countries among developing nations use imported cables and as the life of these cables are of the order of 50 - 75 years, there will be very little scrap coming out of old cables. In India, a certain amount of scrap is available from old cables in addition to the scrap arising out of the cable industry and these are used after simple refining.

Galvanizing is the most important application of zinc among developing countries and good quantities of residues like dross, ash, etc. are available in all countries where galvanizing is in use. Very little scrap or other kinds of residues are available from other applications.

Availability of knowhow

Although the problem of secondary lead and zinc utilization has not been given serious attention in developing countries, there is an increasing realisation among them about the need for efficient utilization of scrap and residues and they are anxious to learn about the possibilities of reclamation of scrap and techniques of winning secondary metals. However, the absence of technical knowhow makes it difficult to establish a stable secondary metal industry. In this context, it will be interesting to digress for a moment and trace the history of development of secondary metals in developed countries. Even in these countries, the secondary metal industries have not grown on systematic and scientific lines and seldom have facilities for research and development. Nevertheless, they have over the years evolved profitable techniques, based mostly on crude investigations by trial and error. These are closely guarded secrets leading to the impression that secondary metal recovery is still more an art than a science. Although in a majority of cases the technique of reclaiming secondary metals is based on simple principles, they need considerable standardization before the process can be exploited on a commercial basis. As a result, even in countries like India where suitable technical personnel are available, the growth of secondary metal industry has been very slow, as industrialists are not inclined to finance any projects that will require any investigation and standardization before their commercial viability can be established. Undoubtedly, this attitude will change gradually when more and more of the scrap will be available at profitable prices when there will be incentives to look for methods of recovery. In developed countries, the secondary metal industry has had ample time for its gradual and progressive improvement. In developing nations, all the industrial progress is confined to the last decade, often called the 'development decade', and it is too soon to expect an established secondary metal industry solely from indigenous resources.

Foreign exchange difficulties

Very few of the developing nations barring Mexico, Peru, Argentina and India are producers of lead and zinc and most of the remaining countries including India import their requirements of lead and zinc. Almost invariably all these countries are faced with problems of foreign exchange, thus making it difficult for them to import these metals. This has led to a chronic shortage of these metals. It may therefore apparently seem that conditions are favourable for the establishment of a secondary metal industry. However, there are numerous inhibiting factors such as lack of knowhow, instability of prices and uncertain supply conditions as a result of which residues are sometimes exported out of the country or not utilised effectively. There are other adverse factors which stifle the development of the secondary metal industry. For instance, most of the galvanizing firms India are keen to reclaim zinc from their residues, dross and ash. However, they are not able to do so because they need some imported components for the equipment and they are unable to obtain these because of foreign exchange restrictions. Therefore, zinc dross is usually sold in the open market and is used in brass making, in spite of the high iron content and part of the ash is exported. There are other possibilities of utilizing scrap and residues with limited import of knowhow and equipment and all these projects have been kept in abeyance mostly as a result of foreign exchange difficulties.

Literature on secondary metals, seminars, symposia, etc.

To develop the secondary metal industry on sound lines, there should be easy and ready access to all the information and literature on the subject. The various development associations and the recently established ZALIS (Zinc and Lead International Service) in developing countries can play an important role in this respect. These organisations are established to provide information and literature on all aspects of zinc and lead including the secondary metal utilization and will specifically serve the local needs of the country. The Indian Office was started 7 years ago and has carried out several programmes aimed at the efficient utilization of scrap and residues. Experience indicates that seminars, symposia and other study group meetings will be very useful. They not only give an opportunity to disseminate knowledge and information but also provide a forum for discussing problems of local interest, identifying the difficulties and attempting collective solutions.

Research and analytical facilities

Given adequate commercial incentives, the secondary metal industry in the normal course will establish itself as a stable commercial sector. However, if this process needs to be hastened, there should be provision for limited research and investigation and other analytical facilities. In this respect, the government can help by providing the necessary grants for these studies and pilot plant investigations and unless these are available, it will be impossible to develop a secondary metal industry quickly, particularly if the country does not want to allow imports of knowhow and equipment. Approach on these lines has been attempted in India but has not been very successful mainly as a result of lack of co-ordination between research and commercial sectors.

Standards

Suitable standards can be formulated to encourage the use of secondary metals. It has been found that unless a standard is available, the industry is reluctant to use secondary metals often under the false impression that they are impure. Furthermore, it is often not appreciated that not all applications need pure metals. Standards for secondary metals should take into consideration the local resources and needs. A beginning in this direction has been made in India in respect of lead and zinc (105, 106).

CONCLUDING REMARKS

In due course, secondary metals will play an important role in the economy of the developing countries in much the same way as in highly developed countries. This, however, is a slow process and in order to quicken the pace effective steps are to be taken and favourable conditions created, some of which have already been discussed. However, it must be recognised that any artificial stimulation of this industry will not bear fruit unless there is primarily an attractive profitability in the secondary metal trade. In most of the developing countries, the economy is not altogether free in the sense that there are numerous controls on import, foreign exchange, etc. Therefore, conditions for the growth of the industry are governed by somewhat different considerations as compared with developed countries, having a free economy. For instance, the respective governments in developing countries may have to make a special study of their resources and needs and create favourable conditions for the speedy establishment of a secondary metal industry. This can be achieved in many ways such as exemption from duty and taxes, subsidies for research and possibly limited help to import certain essential equipment.

Taking an overall view of the developing nations, two basic reasons can be attributed for the present position with regard to secondary metals. Firstly, barring a few countries like India and a few Latin American countries, arisings of scrap and residues are not sufficient to warrant their economic exploitation. Secondly, there has not been adequate time for the natural and spontaneous establishment of a secondary metal industry. Besides, there are other adverse factors such as uncertain supplies, lack of knowhow, erratic prices, etc. Nevertheless, the developing nations should plan ahead so that they are in readiness to exploit the scrap and residues when conditions are favourable. There is, however, a more important aspect of secondary metals which the developing nations should be concerned with and in fact devote more attention to at present. This is with respect to the most efficient and economical use of metals so that very little scrap and residues are produced. While in a number of applications like batteries, scrap is inevitable, in many others like galvanizing, for example, by adopting proper operational techniques the percentage of residues can be kept to a minimum. This is as important as the effective utilisation of secondary metals in terms of the national economy.

Summary

Sources for secondary lead and zinc

Secondary metals are obtained by refining or smelting of scrap and residues. Often the latter are utilized for the direct production of alloys and compounds. Availability of raw materials for secondary lead and zinc depends on the consumption of primary metals for various applications and also on the proportion of scrap or residues arising from each of the end uses. Lead acid batteries and cable sheathing are the chief sources for secondary lead while galvanizing residues, die casting scrap, zinc sheets, etc. are the important sources for secondary zinc.

Reclamation of secondary lead

A major portion of the secondary lead is derived from battery scrap. Their collection is a well organized sector of the secondary metal trade which receives a steady supply of old batteries for the reclamation of lead. Numerous patents and processes are available for the recovery of lead from battery scrap either as a metal or as an alloy of antimony. They include thermal and electrolytic processes, each of which has its own advantages and drawbacks and limited scope of applicability. Strippings of cable sheathing and old sheet and plumbing fixtures are also good sources of secondary lead and the process of refining such a scrap is usually simple. Treatment of other lead bearing residues like dust, fumes, slags, etc. is complicated, very often requiring expensive preliminary processing and complex smelting and refining procedures.

Reclamation of secondary zinc

Although galvanizing residues such as zinc dross, ash, etc. are good sources of secondary zinc, they are often used as raw material for the production of dust, zinc oxide and other compounds of zinc. Production of secondary zinc from galvanizing residues is predominantly confined to thermal techniques although electrolytic processes are also occasionally employed. Zinc sheet scrap is easily processed by simple refining techniques while die casting scrap is usually treated by the same methods adopted for zinc dross. Zinc from flashlight batteries is generally not recovered because of difficulties in collection and separation of the metal.

Economic aspects of secondary lead and zinc utilization

The economics of the recovery of secondary lead and zinc are largely dependent on three important aspects of the secondary metal trade. These include the collection of scrap, the separation of the metallic contents from other ingredients and lastly refining or smelting of the scrap and residues. Each of these stages contributes to the final cost of the secondary metal and there are instances where secondary metal recovery is uneconomical because of excessive cost or practical difficulties attributable to one or more of the above aspects. In addition to these main considerations, factors such as the end uses of the secondary metals, stability of price, freight charges, etc. have an important bearing on the method of utilization of scrap or residues.

Problems pertaining to developing nations

The pattern of consumption of lead and zinc and consequently the scrap utilization in developing areas differ significantly from the highly industrialised countries. Barring a few, good many of the developing nations experience a shortage of the two metals. Thus while apparently conditions are favourable for the reclamation of secondary lead and zinc, there are numerous hampering factors which stand in the way of the establishment of a stable secondary metal industry. These include inadequate and haphazard supply of raw materials, erratic prices, lack of knowhow and equipment and foreign exchange difficulties. However, various steps can be taken to overcome these hurdles. Government assistance and encouragement may be needed particularly in countries which do not have a completely free economy.

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