International Journal of Latest Engineering and Management Research (IJLEMR)
ISSN: 2455-4847
www.ijlemr.com || Volume 02 - Issue 05 || May 2017 || PP. 30-39

"Study and Analysis of lead acid battery recycling process by Pyro-metallurgical Method"

Narendra Kumar Verma[1], Prof.R.P.Kori[2]
[1]*Department of Mechanical Engineering.*
[2]*Department of Mechanical Engineering MITS Gwalior*

Abstract: Lead has the highest rate of recycling of all metals. Because of its corrosion resistance lead scrap is available for recycling decades or even centuries after it is produced. New environmental regulation in many countries has greatly reduced the dissipative uses for lead such as paint leaded gasoline pigments, stabilizers, solder, and ammunition. At present time just under half of the total world lead productions 4.7 million tons come from recycling of scrap materials. There has been very little change in recent years in the percentage of recycled lead only in the past few years has the amount of recycled from scrap materials is expected to increase dramatically in the future

This paper study and production improved the performance of lead acid battery in Recycling Power Plant. In terms of increasing percentage of production, reducing health effect and increasing quality of product lead (Pb). This study approaches the area from two particular perspectives: the impacts of performance and recycling. This technical study is based on increasing production in day to day life approach. The result shows the production and quality improvement with reduced air pollution. Lead acid battery's production can be increased and can be reuse and recycled. Past result of recycling process was observed 80-85% of pure lead in this plant.

After some analysis and modifications implementation of some techniques we observed some improvement of 5-8% in this recycling process and our result climbs to 85-87%

Keywords: Lead; Lead-acid battery recycling, scrape of lead acid battery, process parameter.

I. Introduction

1.1 Introduction of lead (Pb)

Lead is a chemical element in the carbon group with symbol Pb and Atomic number- (82) .lead is a soft, malleable and heavy post transition metal. Metallic lead has a bluish-white color after being freshly cut, but is soon tarnishes to a dull greyish color when exposed to air. Lead has a shiny chrome –silver luster when it is melted into a liquid. It is also the heaviest non-radioactive element (some radioactive, like technetium, are lighter)

Lead use- lead is used in lead acid batteries, bullets and shot,weights,as part of solder ,pewter's, fusible alloys, and as a radiation shield lead has the highest atomic number of all of the stable element. This discussed about the recycling process, recycling parameter and the previous study that involved the optimization technique. Here, the optimization technique Pyro metallurgical Method is review to get fully understanding before applied to the study.

1.2 Recycling process

Recycling in its literal meaning, is the procedure of making used or unwanted products in into new remanufactured products.

The procedure of recycling is unique in the sense that the products are recycled in such a way that the materials that are left after the remanufacturing are considered essential.

When educating one on the process of recycling it helps to remember that most materials can be recycled but certain products (i.e. cell phones and old computers) provide more of a challenge to remanufacture. In this case, the re-making or the reusable materials become much inefficient.

Fig.1

On the other hand, products such as, paper, plastic, glass, tin and some other textiles are all relatively easy for processing and thus the recycling process becomes highly efficient. Easily recyclable items share organic materials just as certain foods and plants do. The procedure that is used in the case of food and plants is known as the composting rather than the recycling.

1.3 The Recycling Process Benefits

The purpose for the recycling is important for a number of reasons. One of the most obvious reasons lies in reducing the amount of natural resources that are consumed for every new product. Since recycling is conserving energy the process.

The recycling process also prevents water as well as air pollution while forbidding the garbage build up accompanied by landfill proliferation. Since materials are brought to a recycling facility they do not wind up in areas that do not have a place for them.

Further, if the procedure of recycling happens to be a perfectly efficient process then one would be able to convert all old wasted products into similar amount of the same product.

Though, there would be an energy expenditure this expenditure is used while processing recycled materials that can raise the cost of manufacturing of certain goods to a higher level.

1.4 Pure lead

Pure lead ingot is being produced from raw lead bullion/remelted and secondary lead ingots/lead scraps through Pyro-metallurgical process. Refining process producing pure lead ingots with a minimum purity level of 99.07% by weight but achieve purity level of 99.975% in most of cases.

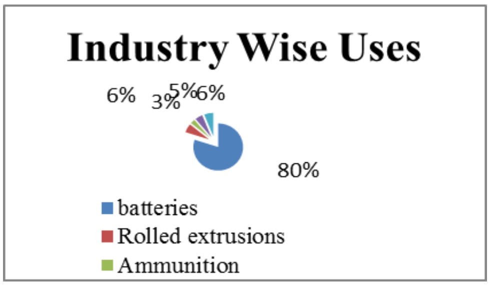

Table 1(industry wise uses)

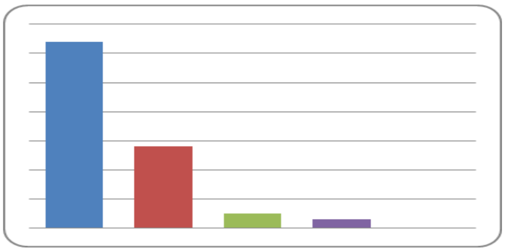

Table 2(Lead acid battery compositions)

Lead-acid batteries are most frequently used in automobiles, boats, and other vehicles. Each battery contains lead and corrosive sulfuric acid electrolyte solution. Smaller sealed lead-acid batteries have been used in computers and cellular telephones.

1.5 Lead Demand & Production

Lead demand during 2011-12 was 410,000 tones as per the Planning Commission, though industry estimates put the figure at much higher levels; this is because of the very large contribution coming from the lead recycling sector, whose number as well as lead imports is not precisely available. The only data that is accurately available pertains to primary lead, produced by Hindustan Zinc Ltd.

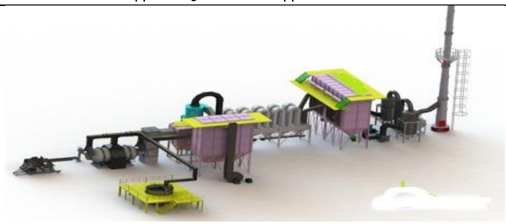

Fig. 2(lead recycling plant)

India's primary lead production during the last few years was as follows and demand next 3 years

Year	demand	Production (tones)
2012-13	600000	60323
2013-14	660000	64319
2014-15	730000	67294
2015-16	800000	76932
2016-17	880000	-------------
2017-18	970000	-------------

Table 3

1.6 Why lead recycling

Lead is a material which is very easy to recycle. It can be re-melted many times, and provided enough processes to remove impurities. The final product (termed as Secondary Lead) is industrial amount of Lead recycled as a proportion of total production is already fairly high worldwide. Over 50% of Lead consumed is derived from recycled or re-used material. Recycling rates of Lead are estimated to be much higher than for other materials.

II. Methodology

We are there discuss about experimental equipment and to be performance of all stage in lead acid battery recycling plant and some implementation of equipment in plant by using Pyro-metallurgical method.

In 2001 the Ministry of Environment and Forests issued the Indian Battery Management and Handling Rules that require lead battery manufacturers to collect a minimum of 90% of the batteries they sell through dealers. The law established an extensive reporting system for dealers, manufacturers, importers, recyclers and others in the supply chain.

Recyclers are also required to be registered by state level pollution control boards. The extensive data collected for compliance with these provisions has never been evaluated or released to the public. Our goal is to evaluate compliance with this rule and its success in establishing large-scale collection of used batteries in India. In particular, we set out to establish if the largest lead battery producers are collecting a sufficient quantity of lead batteries to encourage additional investment and modernization of this highly fragmented industry..

2.1 Pyro-metallurgical method

Pyro-metallurgy is a process through which ores and metals are heated to produce a finished product of workable compounds, purer metals and alloys. The process may be any of the following: drying, roasting, smelting, refining, and alloying, among others. By using high temperatures, one can cause chemical and exothermic reactions in materials. Various methods of heating can be performed, and these can all be referred to as pyro-metallurgy. All processes use heat to change some aspect of the material being worked. The change may be as simple as heating water or other liquids to a gas state and then removing them. Or it could be as complex as chemically bonding metals, such as when copper and tin are combined to make bronze.

Pyro-metallurgical Refining is performed in liquid phase, which means that the crude Lead must be melted to temperatures from 327ºC (Lead fusion point) to 650ºC. As a general trend, the process is performed in batches of 20 to 100 tons, according to the refining plant capacity. The chemical concept behind the refining process is the addition of specific reagents to the molten Lead at proper temperatures. These reagents will then remove the unwanted metals in a specific order as they are added selectively

2.2 Analysis of lead acid battery

Batteries may be hazardous wastes because they contain heavy metals and corrosive electrolyte solutions that are the source of their energy. There are eight metals commonly used in batteries including Lead, Mercury, Nickel, Cadmium, Lithium, Silver, Zinc, and Manganese.

Lead-acid batteries are most frequently used in automobiles, boats, and other vehicles. Each battery contains lead and corrosive sulfuric acid electrolyte solution. Smaller sealed lead-acid batteries have been used in computers and cellular telephones.

The lead-acid battery is a complex industrial product constituted by several materials. The main components of a lead-acid battery are-

1. Active mass
   a) Anode (negative electrode) consisting of Pb
   b) Cathode (positive electrode) consisting of PbO_2
2. Metallic grids, metallic connections
3. Electrolyte (aqueous solution of H_2SO_4)
4. Polypropylene casting (box)
5. Other components (wood, paper, PVC)

By a redox reaction, chemical energy is converted to electrical energy, producing insoluble PbSO4 from Pb and water. The electrode reactions during discharge are following:

Negative Electrode: $Pb + SO_4^{2-}$ e^- $PbSO_4$

Positive Electrode: PbO_2 + 4H+ +SO_4^{2-} + 2e- $PbSO_4 + 2H_2O$

2.3 Lead acid battery recycling plant or working place

Lead recycling plant has been operating a secondary lead recycling plant in Niwari,tikamgarh Madhya Pradesh India since 2011 the technology in 1995 was based upon the use of a short body's rotary furnace which produced approximately 16-20 tons per month of refined lead and lead in alloys.

I was visit in this plant and observed some problems in all the following process and design of plant and structure .so that some implementation in this plant and properly work out in present time regularly

2.4 Scrap or raw materials of lead acid battery

Lead acid batteries are made up of plates, lead and lead oxide with a 35% sulfuric acid and 65% water electrolyte solution. Lead acid batteries represent almost 60%of all batteries sold worldwide.

Fig. 3 Scrap of lead acid battery.

2.5 Classification

Generally there are two types of lead acid batteries, based on their method of construction flooded or sealed. Flooded (or wet) Lead acid batteries are those where the electrodes / plates are immersed in electrolyte. Sealed Lead acid or valve-regulated Lead acid (VRLA) battery where the electrolyte is immobilized. All Lead-acid batteries produce hydrogen and oxygen gas (gassing) at the electrodes during charging through a process called electrolysis. These gases are allowed to escape a flooded cell, however the sealed cell is constructed so that the gases are contained and recombined.

The grid structure in both batteries is made from a Lead alloy. A pure Lead grid structure is not strong enough & therefore other metals like antimony, calcium, tin, and selenium in small quantities are alloyed for added strength and improved electrical properties. The electrolyte in a Lead-acid battery is a dilute solution of sulfuric acid (H2SO4). The negative electrode of a fully charged battery is composed of sponge Lead (Pb) and the positive electrode is composed of Lead dioxide (PbO). The separator is used to electrically isolate the positive and negative electrodes

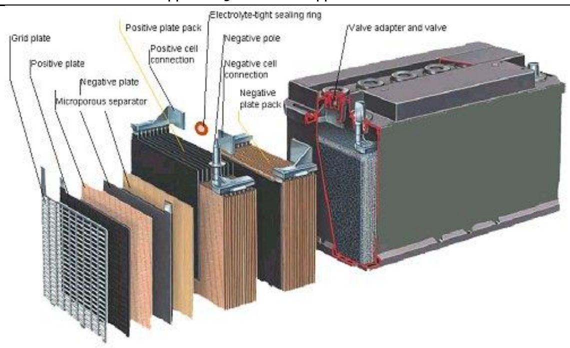

Fig. 4 Parts of lead acid battery

III. Modification and Results

3.1Collected parts of Battery braking stage-

Component	Grids	Battery plates	Separator	Battery case	Acid
Composition	Pb,sb, Ca,Sn	$Pbo_{2,}pbso_4$	Polyethylene glass fiber	polypropylene	$H_2SO_{4,}$Water
%of weight	25-29%	35-55%	3.5-8%	5-8%	11-28%

Table 4

3.2 Air pollution control system

This plant provide the full range of the service for air pollution control The most important aspect of Lead Smelting operation is treatment of effluent gases, which generates by reduction / smelting operation. These pollution control equipment's are designed and tested in house at various degree of operations on various atmospheric conditions. It consists of suitable size Dust collecting chamber (Settling Chamber), Cyclone Separator, Cooling Tower, Ducts, Spark Arrestor, Bag Filter House unit, Wet-Scrubber, Induced Draft Fan and Chimney through which flue gases finally forced out. These pollution control equipment's, are totally, controlled for any kind of over pressure and over temperature. At the inlet of Bag House, Spark Arrestor would be installed, which will catch the sparks coming in the bag house and prevent the burning of Filter Bags. Automatic temperature controlled system at the inlet of bag house is provided

3.3 Pollution control and waste management (Modification in Equipment)

- Dust Collector
- Cyclone
- Cooling Tower (Modification)*
- Spark Arrester
- Bag House (Modification)*
- Wet-Scrubber
- Water Tank(Fitted in the plant)*
- Chimney

3.3.1 Dust collector

It is a sort of Gravity Settling Chamber, the gravity-settling chamber consist of a chamber with baffles in which the gas velocity is reduced to enable dust to settle out by the action of gravity. Here normally the settling of particles larger 100 micron takes place. The velocity of flue gases entering into the dust collector will not be more than 2 m/sec and designed for minimum turbulence in chamber for easy settlement.

3.3.2 Cyclone

It is connected after Dust Collector where flue gas path involves a double vortex with the gas spiraling downward at the outside and upward at the inside. When the gas enters the cyclone, its velocity undergoes redistribution so that the tangential component of velocity increases with decreasing radius. The spiral velocity in a cyclone reaches a value several times the average inlet-gas velocity. These cyclones collect the dust up to the size of 50 Micron.

3.3.3 Cooling tower

It is connected after the Cyclone where the flue gases are allowed to cool down up to 12000^0C to 1300^0C to avoid burning of filter bags. This is properly designed as per the ambient air temperature and based on the heat transfer through conduction and convection. At the bottom of the cooling tower screw conveyor with Rotary air lock valves are provided to collect discharge dust in the bins. If we are modify this cooling process of flue gases, attach a flat plate of metal at the end of passage of flue gases inside the cooling tower some vapors of lead are collected or not delivered with the flue gases to the spark arrester. After this modification, the lead collection is improved.

3.3.4 Spark Arrester

It is also installed after the cooling tower and just before to the bag house to avoid entering any spark into the bag house. Because of any spark, polyester filter bags may get burnt. To avoid such type of problem the spark arrester is designed and fitted before the bag house.

3.3.5 Bag house

Bag House Filtration is a necessary part of today’s Industries. Bughouse is a generic name for Air Pollution Control Equipment (APC) that is designed around the use of engineered fabric filter tubes, envelopes or cartridges in the dust capturing, separation or filtering process. It is present in series, after Spark Arrester and contains filter bags through which dust laden gases passes. Filter bags are made of 100% polyester non-woven fibers with Anti adhesive finish for water repellence and easy dust release with filter cloth and air permeability of 15 m^3/m^2/min. These filter bags are capable to filter 33000 CMH flue gases at temperature of 120^0C-130^0C in the presence of pulse jet cleaning system, which works at the air pressure of 6 kg./cm^2 . Screw Conveyor equipped with Rotary air lock valve is provided at the bottom discharge end for dust removal. In the bag house we have modified the filter bags such as filter bag thickness increase by 1 mm which improves the coal dust particle collection with lead and next in these bags reduce the orifices diameter (distance between the fibers).These modifications have reduced the pollution or emission in the environment and improve the lead collection.

3.3.6 Wet scrubber

It is one of the most essential equipment in the series for controlling pollution mainly removing gaseous pollutants. Counter Current vertically upward flow flue gas against water spray through the packed bad improve efficiency of removal of most unwanted gas from flue gas by water. Mist generated during wet scrubbing action is controlled by mist eliminators present in wet scrubber before flue gas outlet port. The circulating water absorbs Sulfur Di-Oxide gas and the acidic water formed which passes through Water Treatment Plant and gets neutralized. Neutralized water is re-circulated in the system.

3.3.7 Water Tank

Attach water tank between the wet scrubber and chimney the flue gases cool down and lead spread over the water after that it remove by manual process.
This modification improved the lead collection.

3.3.8 Chimney

Chimney is provided for venting flue gases and dispenses pollutants at altitude helping to ease down its influence on surrounding over greater area reducing pollutants concentration in compliance with regulatory limits.

3.4 Analysis of experimental data (Production wise) which found from the lead recycling plant
3.4.1 These data collected of recycling plant or my working place before pre upgrading stage

- Overall per day based calculations-
  Maximum used raw material per day in this plant = 600 kg/day (working time 10 hours)
- Calculated After recycling process –
  Maximum output (pure lead) per day = 483kg/per day (working time 10 hours)
- Approximate recovery of lead around = 80.5%(lead recover after recycling process in percentage)
- Used fuel(coal)

Using the fuel in every step = 57 kg (approximate)

3.4.2 Update/Modified lead recycling plant

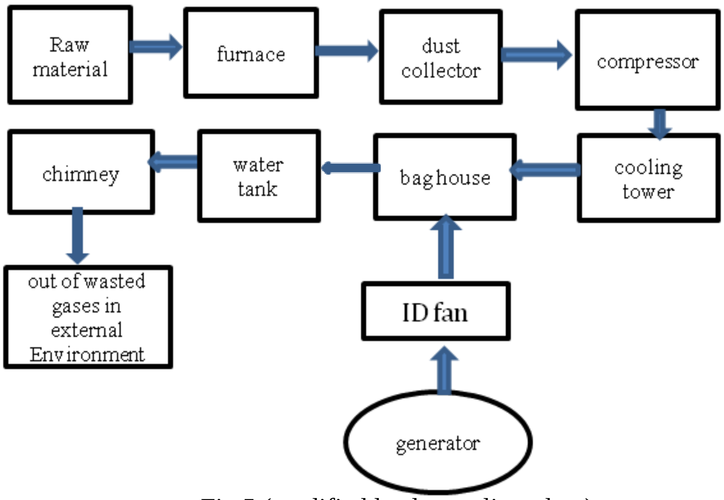

Fig.5 (modified lead recycling plant)

3.4.3 The Practical performance of data in the plant or actual production of lead before modification

Step -1 (Without water tank and any modification)

Used maximum raw material (lead acid batteries) = 600 kg/1 day (10 hour only)

- Calculated After recycling process

Collected actual pure lead after various process = 483.2 kg /1 day (10 hours)

- Approximate recovery of lead around = 80.53 %(lead recover after recycling process in percentage)
- Used fuel(coal)

Using the fuel in every step = 57 kg (approximate)

Step-2 (Without Water tank and modification)

Used maximum raw material (lead acid batteries) = 600 kg/per day (10 hour only)

- Calculated After recycling process

Collected actual lead end of various process = 483.5 kg /per day (10 hours only)

- Approximate recovery of lead around = 80.58%

(Lead recovers after recycling process in percentage)

- Fuel (coal)

Using the fuel in step = 57 kg (approximate)

Step-3 (without Water tank and modification)

- Practically justification

Used maximum raw material (lead acid batteries) = 600 kg/per day (9 hour only)

- Calculated After recycling process

Collected actual lead end of various process = 483.8kg /per day (10 hours only)

- Approximate recovery of lead around = 80.63 %

(Lead recovers after recycling process in percentage)

- Fuel (coal)

Using the fuel in step = 57 kg (approximate)

3.4.4 Practical performance data in the up gradation plant (with water tank and modification)

There is 3 days practical performance in modified plant.

Step -1

- Practically justification

Used maximum raw material (lead acid batteries) = 640 kg/per day

- Calculated After recycling process

Collected actual lead end of various process = 555.3 kg /per day (9 hours 30 minutes only)

- Approximate recovery of lead around = 86.76 %

(Lead recovers after recycling process in percentage)

- Fuel (coal)

Using the fuel in every step = 57kg (approximate)

Step-2

- Practically justification

Used maximum raw material (lead acid batteries) =640 kg/per day (10 hour only)

- Calculated After recycling process

Collected actual lead end of various process = 555.4 kg /per day (8 hours only)

- Approximate recovery of lead around = 86.78 %

(Lead recovers after recycling process in percentage)

- Fuel (coal)

Using the fuel in step = 57 kg (approximate)

Step-3

- Practically justification

Used maximum raw material (lead acid batteries) = 640 kg/per day (10 hour only)

- Calculated After recycling process

Collected actual lead end of various process = 556 kg /per day (10 hours only)

- Approximate recovery of lead around = 86.87 %

(Lead recovers after recycling process in percentage)

- Fuel (coal)

Using the fuel in step = 57 kg (approximate)

"*These data collected of lead recycling plant or my working place after up gradation*"

3.5 Profit-

3.5.1Total Profit privies stage -

Pure lead marketing cost in Indian Currency - 112-118 Rs./kg

- Before modified plant provided pure lead every day = 483 kg

Total production of every day = 483*112
= 54096 Rs.

Total cost (labor, raw material, maintenance)
= 49730 Rs.

Total actual profit per day basis = **4366 Rs.**

3.5.2Total Profit plant up gradation stage -

- After modified plant pure lead collected every day = 555 kg

Total production of every day = 555*112
= 62160 Rs.

Total cost (labor, raw material, mainte.) =53800 Rs.

Total actual profit per day basis = **8360 Rs**.

3.6 Capacity improvement

Pre upgrading plant capacity = 600 kg/per day

Upgrading plant capacity increase = 640 kg /per day

3.7 Advantages of modification plant

- Raw material saving
- Scrap losses decrease
- Increase no of working days
- Layout modification
- Process modification
- Time reduction
- Higher profits.
- Low labor costs.
- 99%+ Lead yield.
- Low energy costs.
- Environment Friendly.

- Reduced processing cost per ton.
- Simplified environmental compliance.
- Reduces the market demand supply Gap.

3.8 Analysis of Quality wise improvement

3.8.1 Pure lead (percentage of all included elements) in pre up gradation plant-

Element	Symbol	Composition in %
Antimony	Sb	0.001(max.)
Arsenic	As	0.001(max.)
Tin	Sn	0.001(max.)
Copper	Cu	0.001(max.)
Bismuth	Bi	0.025(max.)
Iron	Fe	0.001(max.)
Nickel	Ni	0.001(max.)
Silver	Ag	0.003(max.)
Zinc	Zn	0.001(max.)
Calcium	Ca	0.0005(max.)
Sulphur	S	0.0005(max.)
Aluminum	Al	0.0005(max.)
Selenium	Se	0.0005(max.)
Cadmium	Cd	0.0005(max.)
Tellurium	Te	0.0010(max.)
Lead	Pb	99.070(min.)

Table No. 5

3.8.2 Pure lead (percentage of all included elements) in modified plant

Element	Symbol	Composition in %
Antimony	Sb	0.001(max.)
Arsenic	As	0.001(max.)
Tin	Sn	0.001(max.)
Copper	Cu	0.001(max.)
Bismuth	Bi	0.025(max.)
Iron	Fe	0.001(max.)
Nickel	Ni	0.001(max.)
Silver	Ag	0.003(max.)
Zinc	Zn	0.001(max.)
Calcium	Ca	0.0005(max.)
Sulphur	S	0.0005(max.)
Aluminum	Al	0.0005(max.)
Selenium	Se	0.0005(max.)
Cadmium	Cd	0.0005(max.)
Tellurium	Te	0.0010(max.)
Lead	Pb	99.970(min.)

Table No.6

IV. Conclusion

Lead-acid battery recycling could benefit both lead pollution control and resource recovery. Great efforts have been taken in India and some developing countries to improve lead recovery from waste lead-acid battery treatment.

After successful implementation of the method and modifications in the process by usung a water tank ,we able to increase the recycling percentage of lead upto 86-87% (previously it was in the range 80-83%). By this method we also increase the purity of lead as mentioned in the table - .

The percentage of lead emitted through the chimney into the atmosphere is also reduced thus helping in pollution control. Overall capacity of the plant is also increased from 600 Kg/Day to 640 Kg/Day

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