Battery Recycling

LEAD RECLAMATION FROM SPENT BATTERIES

1. SIGNIFICANCE OF LEAD-ACID BATTER RECYCLING

Lead-acid batteries are the environmental success story of our time. More than 98 percent of all battery lead is recycled. Compared to 55% of aluminum, 45% of newspapers, 26% of glass bottles and 26% of tires, lead-acid batteries top the list of the most highly recycled consumer product.

The lead-acid battery gains its environmental edge from its closed-loop life cycle. The typical new lead-acid battery contains 60 to 80 percent recycled lead and plastic. When a spent battery is collected, it is sent to a permitted recycler where, under strict environmental regulations, the lead and plastic are reclaimed and sent to a new battery manufacturer.

The recycling cycle goes on indefinitely. That means the lead and plastic in the lead-acid battery in your car, truck, boat or motorcycle have been — and will continue to be — recycled many, many times.

This makes lead-acid battery disposal extremely successful from both environmental and cost perspectives.

Lead-acid batteries are essentially 100% recyclable. During the recycling process, a battery is separated into three distinct components. The lead is smelted and refined to be used in new batteries. The plastic case is recovered and its material cleaned, and molded into new battery cases, the used acid is even recycled for reuse.

The Lead Acid Battery Recycling involves in the collection of the spent batteries from various sources, which are transported to the Recycling facility through a certified logistics system. This transportation is essential to avoid the contamination of the environment by the spent batteries and their constituents. The transported Batteries are processed in the Recycling Facility for the Production of Lead Ingots, the raw material for the production of new batteries and the cycle progress repeatedly.

2. LEAD ACID BATTERIES

The storage battery or secondary battery is such battery where electrical energy can be stored as chemical energy and this chemical energy is then converted to electrical energy as when required. The conversion of electrical energy into chemical energy by applying external electrical source is known as charging of battery, whereas conversion of chemical energy into electrical energy for supplying the external load is known as discharging of secondary battery. During charging of battery, electric current is passed through it which causes some chemical changes inside the battery, this chemical changes absorb energy during their formation. When the battery is connected to the external load, the chemical changes take place in reverse direction, during which the absorbed energy is released as electrical energy and supplied to the load.

The Following are the Important Recyclable Parts of the Lead Acid Battery:
- Battery Cases and Covers
- Posts and Terminal (Pure Lead)
- Battery Grids (Cathode and Anode)
- Electrolyte with Lead Paste

The above mentioned parts are explained clearly in the Fig No. 1. Out of the above listed components lead can be recycled from the posts, terminals, Battery Grids and the Electrolyte containing the Lead Paste. The posts and the terminals of the battery are made up of pure lead and they can be directly smelted to produce Lead which is a good option in manual separation of the battery.

Table No. 1: Chemical Composition of a Lead Acid Battery.

<table>
<thead>
<tr>
<th>Chemical Composition by weight</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Metallic Lead (Poles and Terminals)</td>
<td>25 – 30</td>
</tr>
<tr>
<td>Electrode paste (fine particles of Lead oxide and Lead sulphate)</td>
<td>35-45</td>
</tr>
<tr>
<td>Sulphuric acid (10 – 20 % H2SO4)</td>
<td>10-15</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>5-8</td>
</tr>
<tr>
<td>Other plastics (PVC, PE, etc.)</td>
<td>4-7</td>
</tr>
<tr>
<td>Others materials (glass, etc.)</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
3. MAIN STAGES OF LEAD ACID BATTERY RECYCLING

The batteries that are collected by the above method are stored in a safe place for further processing which involves in the treatment of all the constituents of the battery. The three main stages of Lead Acid Battery Recycling are

- Battery Treatment
- Smelting and
- Refining

3. 1. BATTERY TREATMENT

Batteries are typically unloaded by hand from trailers, conveyors, or from pallets. The batteries are then prepared for smelting by draining the acid and separating the plates, rubber, plastic containers, and sludge. The first process involved in the Battery Treatment is the breaking of the battery and loading the constituents into the separation unit. This separation can be done based on the scale of the production and the safety standards that required to be followed for the Facility and the Man power. The Battery Breaking Process can be done in three ways, they are enumerated below with their description and effects.

1. I. Manual Battery Breaking
2. Semi-Automatic or Industrial Battery Breaking and
3. Automatic Battery Breaking.

3.1.1. INDUSTRIAL BATTERY BREAKING

The “manual” technique is not used by many Lead Recycling Facilities. After the battery passes through the saw or shear, an employee manually dumps the “groups” or lead-bearing material into a pile and places the case and top of the battery into another pile or conveyance system. This process is vulnerable to the exposure of the constituents in the battery to the environment. This method is limited to small scale processing as large scale processing requires sophisticated method and increased manpower. A few effects that can be observed during the Manual Battery Breaking is as follows,

- Splashes of lead-laden liquid may dry on equipment and adjacent surfaces and become airborne through re-entertainment or physical disturbance.
- Lead-laden acid mist may be created from the physical dumping of batteries.
- Acid mist may be generated by the saw or shear, which is located in close proximity to the dumping station.

3.1.2. INDUSTRIAL BATTERY BREAKING

Industrial batteries, used to power mobile electric equipment or for other industrial uses, are periodically purchased for raw material by most secondary smelters. Many of these batteries have steel cases which require removal by cutting the case open with a cutting torch, a hand-held gas powered saw, or other equipment that can separate the case from its contents. Though this is an important method of recycling batteries, it is not applied in the processing of the spent Automotive Batteries.
3.1.3. AUTOMATIC BATTERY BREAKING

The four most common processes for breaking automotive batteries are:

- High speed saw
- Slow speed saw
- Shear
- Whole battery crushing

The use of saws and shears involves cutting the tops off of the batteries, then dumping the contents of the battery. The whole battery crushing process involves crushing the entire battery in a crusher, shredder or hammer mill, and separating the components by gravity separation. This is the most suitable method of breaking the batteries in a Large Scale recycling of the batteries as the time scale of the operation is more important for the overall output of the system. This system requires manual loading of the batteries in the conveyor and then the system operates in the following way,

- Through an inclined conveyor, the batteries are transported into the cutting machine.
- Conveyor Band Saw Cutting machine is used to cut the top portion of the battery.
- The saw is designed with adjustable height in order to accommodate different types of batteries, after sawing the battery will be released and the lid will be removed manually, the lead plugs and anodes will be removed from the battery by applying a hammer.

After cutting the battery is fed into a hammer-mill or crushing-mill which breaks the battery into small pieces of about 50mm in cross sections, this crushed material includes all the essential constituents of the battery and indicates the beginning of the battery recycling process. There is one more option available in this method of separation, the poles and the terminals of the battery made of pure lead can be removed and directly fed for smelting without being processed together with all the other parts where the concentration of lead varies. During this crushing the first phase of the separation of the electrolyte (acid) is done. The crushed substances are then passed through a series of sieves where the battery paste and remaining electrolyte are removed. This is the point of diversion of the lead substance and electrolyte with lead paste for different processing methods, the plastic and the lead fragments remaining in the sieve’s are loaded to another separator where the materials separated by the Sink/Float process to remove the plastic form the Lead for further processing of the Lead fragments. The operating principle of the Sink/Float is based on the water stream that keeps the lighter plastics floating on the surface and letting the lead fragments fall so that they can be collected by the effect of gravity. This water jet is obtained be pumping the water upwards through the bottom of the floating basin. The water stream is regulated in order to adjust the process capacity for various densities of the items. The Sink/float is fed at the top through the conveyor and the heavier lead parts settle at the bottom, which are collected through Screw Conveyor. The plastic parts that are collected through this method still contains a quantity of the lead paste which can be washed away and fed to the desulphurization equipment where the Sulphates of Lead is reduced to Lead and Lead Oxide, the required end product.
3. 2. SMELTING

The Lead to be processed is obtained in two forms after the separation, one form is the pure lead (poles and terminals) and the grids and the other form is the lead paste mixed in the electrolyte. The difference in these two forms requires two different methods by which the Lead from the spent battery can be recycled. The reactions involved in the smelting of lead is,

\[
Pb_3O_4 + CO \rightarrow 3PbO + CO_2
\]

\[
2PbO + 2CO \rightarrow Pb_2 + 2CO_2
\]

The reduction of lead as mentioned above takes place at a higher temperature in the presence of Carbon monoxide which reduces the Lead Tetra oxide (Pb3O4) into Lead monoxide (PbO) and again reduces to lead. The constituent inside the smelting furnace still contains the compounds of sulphates that require additional treatment.

The pole, terminals and the grids obtained from the battery with minimum impurities are melted in a smelting furnace where the temperature is maintained at around 1200º C. The smelting furnace is normally a rotary furnace where the lead elements are fed from one side and heated. Since the furnace is rotating the heaviest lead in liquid form settles in the bottom, which is removed through the specific outlets designed for the transmission of the lead. The lead obtained from this furnace still contains a trace amount of impurities that needs to be refined to get the industry grade Lead. The drust (impurities) that are formed in the surface of the rotary furnaces are collected through dust collectors which is a mixture of SOx and other pollutants that are harmful for the surroundings. These are processed through the cyclone separator, cooling tower and bag house filter to collect the Sulphur content in the exhaust that leaves only CO2 to be vented to the atmosphere.

The Lead obtained from this process is called as Hard Lead due to the metallic impurities. The lead is classified into two types, they are i) Soft Lead and ii) Hard Lead based on the purity of the lead and the percentage of metallic impurities. The property of soft lead is that the purity in terms of percentage should not be less than 99.97. Added to that there is a standard percentage of metallic impurities that should not exceed which is described in the Table. No. 2. Along with hard lead dross is also formed during smelting this dross is usually a mixture of the metallic impurities which are treated in the refining to filter them as by-products.

The pollutants formed during the smelting of lead is processed in the following equipments to filter the environmental pollutants and treat the pollutants of lead acid battery recycling to keep the emission levels within the environmental standards.

- Dust Collector
- Cyclone
- Cooling Tower
- Spark arrestor
- Bag Filters
- Wet Scrubber
3.2.1. DESULPHURIZATION

The electrolyte with the lead paste is essentially a mixture of Sulphuric Acid (H2SO4) and lead sulphate (PbSO4) and other constituent, the main function of this process is to convert this lead sulphate into lead carbonate which in turn can be smelted to form the lead metal. This conversion of the lead sulphate to lead oxide is done in a desulphurization chamber where the sulphates from the lead is removed at a lower temperature of about 600o C. This reaction is done with a carbonate (can be Na, NH3 etc) is converted into sulphate whereas the lead is converted into lead carbonate which can be smelted and processed.

\[
PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4
\]

The treatment of a carbonate with the lead sulphate reduces the requirement of high temperature during calcinations which normally takes place at a temperature of 1400o C. The calcinations of the lead carbonate is done at a temperature of 600o C, this breaks the lead carbonate into lead oxide and carbon-dioxide.

\[
PbCO_3 \rightarrow PbO + CO_2
\]

This lead oxide obtained from the desulphurization chamber is fed to the smelting furnace for the conversion into Hard Lead. Desulphurization involves in the treatment of lead sulphate with a solution of a carbonate and the resulting product, i.e. sulphate is in a huge quantity which must be treated either within the recycling plant or in other processing facility.

3.3. REFINING

The metallic lead produced by the above process contains a number of impurities, which will affect the performance of the lead during usage after recycling to eliminate this metallic lead obtained from the smelting furnace to be refined in a kettle to reduce the amount of these impurities and increase the quality of the Lead produced. The Lead metal produced is expected to be 99.97% pure, the important impurities that must be reduced are Copper, Tin, Antimony and Arsenic. Pure Lead Ingot produced from Lead Metallic Scrap through Pyrometallurgical desulphurization method. At the Refining Process, the produced Pure Lead Ingots should be with a minimum purity level of 99.97% by weight that in mostly achieves purity level of 99.985%.
The Standardized composition of the Pure Lead Ingot is explained in the following table.

Table No. 2: Chemical Composition of Soft Lead

<table>
<thead>
<tr>
<th>Elements</th>
<th>Composition in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (Pb)</td>
<td>99.970 (min)</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Bismuth (Bi)</td>
<td>0.030 (max)</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>0.005 (max)</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.001 (max)</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.0005 (max)</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>0.0005 (max)</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>0.0005 (max)</td>
</tr>
</tbody>
</table>

The process of refining in a kettle involves a sequence of events to remove all the metallic impurities on by one to form Soft Lead. All the above mentioned metallic impurities are removed by various chemical and heat treatment reactions. The first metallic impurity removed in the refining is Copper; the hard lead is melted and allowed to cool to a temperature above the melting point of lead. The Copper crystallizes and rises to the surface where it is skimmed off as a Copper-rich surface dross. Sulphur is stirred into the molten lead to reduce the copper content by forming Copper Sulphide, skimmed off from the surface of molten lead. There are two methods to process the lead from this stage i) Electrolysis where the pure lead deposits in the lead cathode and the impurities remain on the anodes, ii) Pyrometallurgical process. In pyrometallurgical process, the metallic mixture obtained after copper removal is sequentially heated and cooled under different conditions and temperatures. These processes either oxidize or remove the metal impurities from the refined lead. The various sequential process involved in this pyrometallurgical process are:
3.3.1. DESULPHURIZATION

The presence of arsenic, tin and antimony causes lead to be hard, this is removed to soften the lead by melting and agitating with an air blast. In this process a flux of molten sodium hydroxide and sodium nitrate is added to the lead. After thorough mixing arsenic, tin and antimony impurities are removed in an alkaline flux as sodium arsenate, stannate and antimonite.

3.3.2. DESILVERISING

This process removes the silver and gold by the addition of zinc in the kettle. Silver and Gold dissolve in the zinc, which being lighter than lead rises to the surface. The temperature of the molten metal is lowered and the silver and Zinc dross solidifies and skimmed off and the zinc is again used in the desilverising process.

3.3.3. ZINC REMOVAL

A vacuum is created over the surface of the molten metal and the zinc vapour condenses over the dome of the vacuum vessel. The Zinc is collected and reused in the desilverising process.

3.3.4. BISMUTH REMOVAL

When a calcium magnesium alloy is added to the molten lead, Bismuth forms a more complex alloy which rises to the top of the metal and it is skimmed off.

3.3.5. FINAL REFINING

The addition of caustic soda to the molten lead at high temperature leads to the formation of a dross of sodium antimonite and zincates which is removed from the surface. The above mentioned processes are combined together to refine the lead and the resulting lead is cast into ingots. The drosses obtained from the refining process are re-smelted to obtain the impurity as a by-product and to recover lead contained in them. Copper drosses are treated and sold for the recovery of copper. Antimony and Tin are recovered in the form of concentrated alloys with lead and used for the preparation of other lead alloys for example tin-lead alloy is used in the preparation of solder. The final process in the lead acid battery recycling is the casting of the refined molten lead into Ingots in the casting machine.
4. ELECTROLYTE AND POLYPROPYLENE

The other constituents obtained from lead acid battery recycling are the i) Electrolyte largely in the form of Sulphuric acid (H2SO4) solution and ii) Polypropylene from the cases and covers. The Sulphuric acid from the battery is of 18% concentration, which can be reused in the production of new batteries by chemical retreatment i.e. increasing the concentration of the acid for reuse. Otherwise the sodium sulphate crystals from dilute sulphuric acid are resold to textiles and detergent manufacturing. Effective treatment of this sulphuric acid with other solutions can yield raw materials for the production of fertilizers in agriculture. The Plastic pellets from the polypropylene cases are reused to produce new cases and covers for new batteries.

5. REFERENCES

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4. “Controlling Lead exposures in the Construction Industry: Engineering and Work Practice Controls” – Occupation Safety and Health Administration, USA