Secondary Lead Smelting as an Integral Part of Battery Manufacturing

R. A. Leiby, Jr.
Vice President, Metals Operations
East Penn Manufacturing
Lyons, PA 19536

Mark Bricker
Assistant Plant Manager, Smelter
East Penn Manufacturing
Lyons, PA 19536

Abstract
Secondary lead smelting operations at East Penn's captive smelter have been previously described by Pike (1990)[1] and Leiby (1993 & 2005).[23] Since that time, operational changes at EPM have focused on achievement of compliance with strict environmental regulation and the recycling of all the components of spent batteries to the supply of raw materials for the manufacture of new batteries. While achieving desired sustainability, the recycling of Lead, polypropylene, and sulfuric acid directly to the battery manufacturing process allows EPM to further capitalize on the vertical integration of its Lyons, PA manufacturing campus.

Introduction
East Penn Manufacturing Co., Inc. (EPM) is a producer of lead-acid batteries and associated products. The Lyons, PA manufacturing campus encompasses over 520 acres incorporating six battery manufacturing facilities, two injection molding facilities, two lead oxide facilities, a secondary lead smelter, and associated support operations The smelter represents, through a closed-loop approach, a commitment to product stewardship and environmental protection. The smelter processes an average of 6 million batteries per year, recycling virtually 100% of each spent battery received for processing. This results in the recovery of 100,000 tons of lead, 5,000 tons of polypropylene, and the equivalent of 3,500 tons of 92% sulfuric acid on an annual basis.

Smelter Process
Overview
Figure 1 provides the flow sheet of the smelting operations. Items in red are returned to battery manufacturing, blue are sold as products, green are internally reused, and purple are discarded. The smelting technology employed is conventional pyrometallurgy utilizing a reverberatory furnace and a blast furnace (cupola) to recover the metal. The off gases from these furnaces are combined for the gas cleaning process. There are some aspects of this process that are unique to EPM. A patented a process for the recovery of sulfuric acid from spent batteries is utilized. This solvent extraction process removes impurities to obtain acid which is then used in the acid mixing departments of the battery plants. Additionally, the process does not utilize a soda ash leach circuit to convert lead sulfate paste to lead carbonate prior to smelting while recovering the sulfur as sodium sulfate. Instead sulfur is converted to SO_2 in the gas stream and subsequently scrubbed with ammonia to recover a saleable solution for the manufacture of liquid fertilizer. Finally, the waste water treatment facility combines conventional and advanced technologies to allow reuse of treated water to the manufacturing process.

Throughout the process, enclosure and ventilation are employed to control both process and fugitive emissions. Baghouses are equipped with polytetrafluoroethylene (PTFE) membrane bags followed by High -Efficiency Particulate Air (HEPA) filtration or scrubbing to reduce stack emissions. Hygiene ventilation, isolation, HEPA filtration of specific areas, along with proper work practice controls, housekeeping, personal protective equipment, personal hygiene practices, and employee incentives are used to maintain reduced employee exposures to toxic metals.

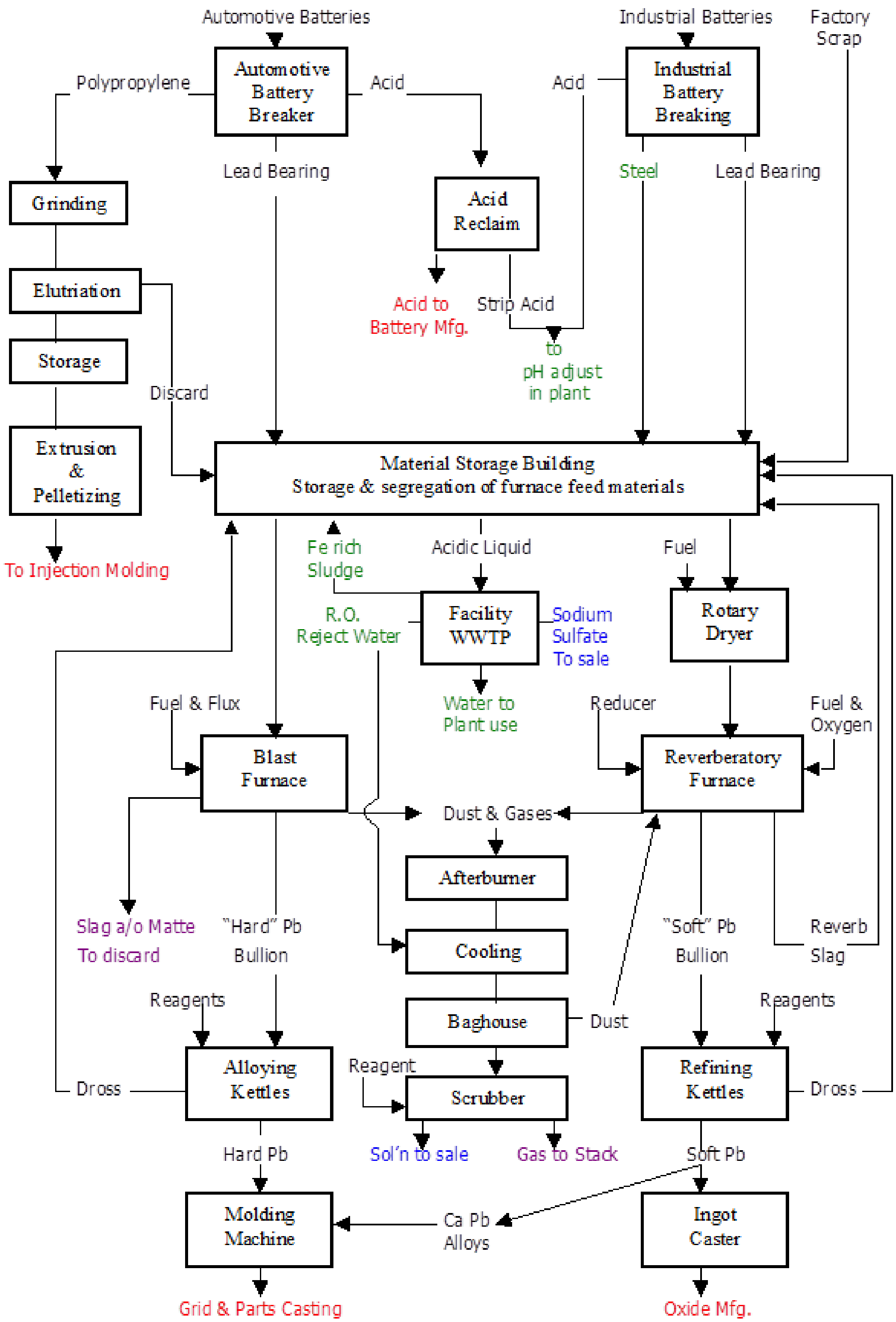

Figure 1. EPM Secondary Lead Smelter Process Flow Sheet.

Battery Receiving

The battery receiving area consists of 4 dock locations allowing the inspection and unloading of full trailer load quantities of spent lead acid batteries. The spent batteries can be offloaded and directly conveyed to the dismantling process. Also included is an area compliant with the Federal regulations regarding containment buildings allowing for the storage of up to 100,000 units ahead of dismantling. Skids of batteries are stored for future processing in a high density flow rack system manufactured by Engineered Products of Greenville, SC. Receiving includes an automated sorting process for the empty pallets returned from dismantling providing shredding of unwanted pallets and sorting and stacking of desirable pallets to be returned for repair and or reuse in the facility.

Figure 2. High density storage of spent lead acid batteries.

Battery Dismantling

Automotive spent battery dismantling is accomplished with a modified MA Engineering model 61 total separation system which crushes the batteries and separates the components via a sink/float system. The pallets of batteries after unloading from trucks are conveyed to a dumping station where they are unloaded into an apron feeder in a semi- automated process. The batteries are singulated onto a conveyor belt and undergo visual inspection for alternative chemistries. They then pass through a rotary shear shredder manufactured by Shredding Systems Inc. and across a Carrier Conveyor vibratory deck to facilitate the removal and collection of spent sulfuric acid and finally into the hammermill ahead of the sink/float. Solids are removed from the acid by means of a settling screw and combined with the lead sulfate slurry discharge from the process.

The discharges of metallic lead and polyethylene separators are collected in a Hapman Conveyor Co. tubular drag conveyor and conveyed directly to the material storage room. The lead sulfate slurry is pumped into one of two 1.5 X 2 meter plate and frame filter presses manufactured by Andritz Inc. Each press has 82 chambers with a potential cake thickness of 50 mm resulting in a filter volume of 9.9 cubic meters.

The polypropylene fraction is washed and dried in two spin washers manufactured by Gala Industries and size reduced in two Cumberland Engineering Corporation model X1000 granulators each capable of handling 3,000 pounds at a size of 5/8”, then air classified to remove any residual polyethylene or label material and conveyed into two storage silos. Presently the dismantling process is operated two shifts per day five days per week providing the required feed materials for furnace operations.

Motive power, stationary and locomotive batteries are dismantled by means of a Model 6000-HD / 400 HP dual drive hydraulic rotary shear shredder. The process utilizes a vibratory deck for acid separation and recovery and magnetic separation to remove tramp iron. This unit can process varying sizes and configurations of batteries including steel tray motive power batteries up to 12 cells in size. The tramp steel is used for its iron content as a slag constituent in the blast furnace.

Material Storage Building

The material storage building was upgraded to meet the Federal “containment building” regulations in 1994. The building floor includes secondary containment and leak detection beneath a wear surface of concrete covered with acid resistant brick lain on a chemically resistant membrane that is carried four feet up the walls. The working surface slopes to a collection sump. All lead bearing materials destine for processing through the furnaces are conveyed into the room by conveyors, skip hoist, or specialized dump areas. Furnace feed apron conveyors are located adjacent to and are filled from the storage building. Materials within the room are handled by means of a Caterpillar Model 924 front end loader, equipped with HEPA filtration on the cab.

Polypropylene Recycling

An extrusion line for the recovery of polypropylene into battery grade polypropylene for use in EPM’s injection molding operations was started in 1998. The line consists of a pneumatic conveying system which transfers the material from storage silos to a Maguire Products weigh scale blender mounted to the throat of a 165mm Davis-Standard Corporation Thermatic™ extruder. A Bovram model CLF screen changer is used to filter the extruded polypropylene prior to a Gala Industries Inc. 7SLC underwater pelletizer which produces the final product. The pellets are passed through a vibrating screen to eliminate any potential oversized material and then pneumatically conveyed directly to the storage silos at injection molding. The process is controlled by a Davis Standard Epic III control system.

Figure 3. Plastic extruder, screen changer, pelletizer, and controls.

Acid refining

Acid refining operations were previously described in detail by Leiby, Spitz, and Bricker (1995 & 2000).[4,5]This solvent extraction method combined with electrochemistry has continued to be practiced as described. In 2000 the original reagent was completely replaced. Since that time, periodic additions have been made for volume correction only. Since 2000 the equivalent of over 50,000 tons of 92% sulfuric acid has been recovered.

Reverberatory Furnace

The primary smelting furnace is the reverberatory furnace. The lead bearing feed materials are dried prior to the furnace by means of a HeylPat Corporation rotary dryer which is seven feet in diameter and 40 feet long. Feed materials are placed in an apron feeder which feeds a skip hoist which in turn feed a screw conveyor discharging material into the dryer. The dryer is equipped with both lifters and flights to turn the material as it passes down the length of the kiln. A 13 million Btu conventional burner provides hot air which travels co-current to the feed material. Burner operation is modulated to maintain a set discharge temperature. Material enters the dryer at approximately 12% moisture and is discharged containing <1%. The dryer breachings utilize labyrinth type seals under positive pressure to prevent leakage. Material exiting the dryer is collected in a screw conveyor that in turn feeds an inclined screw conveyor extending to the roof of the furnace. The material then passes through a Platco Inc. double tipping valve which acts as an airlock and then through a water-jacketed opening in the roof. The dryer is maintained under negative pressure by means of a Scientific pulse jet baghouse equipped with polytetrafluorethylene (PTFE) membrane on PTFE felt bags. The collected particulate is discharged to the feed screw to the furnace.

The furnace is 28 feet long by 8.5 feet wide at the slag line. The refractory is direct bonded chrome-magnesite brick and the hung roof constructed of metal clad basic brick. Water jackets are used at the slag tap, the pusher feeder, the roof opening, and the roof of the transition to the afterburner. In addition, the copper burner blocks on the furnace are water cooled. The jackets are cooled by a totally enclosed, pressurized, recirculating cooling fluid system circulating a 40% propylene glycol and water solution. The solution circulates from a 675 gpm pumping station to the jackets and returns to a liquid to air heat exchanger. Liquid temperature averages 140^{o} F.

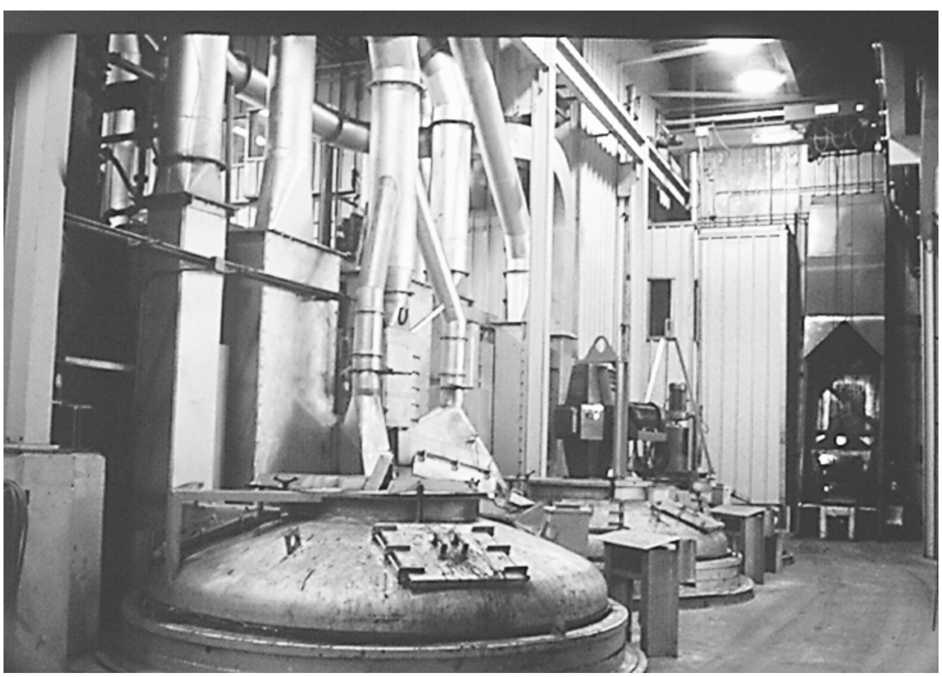

Figure 4. Reverberatory furnace, lead well and holding kettles.

The furnace is fired with an American Combustion (Air Liquide) Pyretron® burner system. Six burners, two on the feed end wall and four on the side walls provide a maximum of 31 million Btu of heat input. The burners are fueled by natural gas. Oxygen is supplied by an onsite Praxair Linde OxyGen® vacuum pressure swing adsorbtion system. Each burner is mounted on a water cooled copper burner block. Burner operation and control is incorporated in a custom control system created by Advanced Automation Associates, Inc. that encompasses charging rates, burner operations, process temperatures and off gas handling.

The lead bearing material introduced to the furnace sits on a drying shelf where it is heated by both radiant and convection from the hot gases and the furnace walls. Most of the chemical reactions occur in the first half of the furnace while the remainder is utilized to separate the slag from the bullion. The principal object is to oxidize the sulfur to SO_2 and eliminate it to the gas stream while the alloying agents (antimony, arsenic, and tin) are oxidized to produce a slag concentrating those elements. These reactions have been reported by R. D. Prengeman in 1980.[6] Lead compounds are reduced to metallic lead and flow from the furnace via the lead well into holding kettles for preliminary treatment and refining. This clean “soft” bullion is then transferred by means of a pump to the refinery kettles. Slag continuously flows through the slag notch and is cast into 2400 pound blocks to be transferred to the material storage building to become feed for the cupola. Typically one ton of slag is produced for every 3 tons of bullion.

Blast Furnace (Cupola)

The blast furnace is rectangular in shape 38” X 62” at the tuyeres and 63” X 62” at the top. The column is 15 feet high with 5° of bosh on the sides only. Ten rectangular tuyeres equipped with automated Eurotherm 3508 air weight controls and automated tuyere punchers deliver the air from one of two Stutorbuilt 8L positive displacement blowers. The furnace column is a water jacket on a closed loop cooling system equipped with a liquid to air Colemac coil dry cooler and two ITT, Inc. pumps. The top of the column is closed by a thimble and off gas is removed through a side take off. The bottom of the furnace is a removable refractory lined crucible equipped with a lead well and a water cooled slag tapping block.

Figure 5. Tapping Slag from the cupola.

The charge for the furnace consists of coke, fluxes, and lead bearing feed which is principally reverberatory furnace slag, dross, industrial cells, and battery plant scraps. These lead bearing materials are mixed to yield bullion containing antimony close to top lead specification. Feed materials are weighed in an automated system, and introduced into the furnace through the thimble as layers. Controls were developed by EPM's controls group.

"Hard" Lead bullion flows from the lead well to a rotary casting table producing 2600 pound ingots for the refinery. Slag is tapped intermittently as it appears at the tuyeres into one ton molds which are then cooled and dumped into a separate enclosure for further cooling, loading into dump trailers and finally transport to landfill for disposal as hazardous waste.

Furnace Gas Handling System

The cupola gases pass through a 60° incline pipe and are comingled with the reverberatory furnace gases close to the exit of the reverberatory furnace and prior to entering an afterburner. Inside the refractory lined afterburner the gas temperature is maintained above 1400°F whenever the furnaces are operating to remove all of the organics from the off gas. The gases then are cooled to 320°F by evaporative cooling, a series of radiant cooling tubes and the addition of local exhaust ventilation air prior to entering a baghouse.

The process baghouse is a Wheelabrator mechanical shake baghouse with six cells dedicated to the furnace gases. The cells employ 8.5 oz. Gore-Tex® membrane (PTFE) on Gore-Tex® fabric with an air to cloth ration of 1.5:1. The gases then pass to an ammonia scrubber designed by A. W. Spitz & Associates. The gases are scrubbed in a two stage process where pH and specific gravity are closely monitored and controlled. Batches of Nitrogen-Sulfur (NS) solution are made containing 8% Nitrogen and 12% Sulfur which are then sold as a raw material for the production of liquid fertilizer. The gases are then passed through a Monsanto Enviro-Chem mist eliminator capable of filtering 60,000 ACFM at 8" w.g. of pressure drop prior to discharge to atmosphere. Liquid collected from the mist eliminators is returned to the scrubbing process.

Lead Refining

Secondary soft lead is produced from the clean reverberatory furnace bullion by the removal of any residual antimony with sodium nitrate, followed by the removal of nickel and copper through the use of iron pyrite and sulfur, and finally tellurium is removed through the use of potassium hydroxide. The final metal when in specification is cast as one ton blocks in ten water cooled ingot molds. Removal is accomplished with an Anver Corporation Model VPF-3 electric vacuum lifter on a jib crane.

Calcium lead alloys are manufactured starting with soft lead and alloying the elements into specification using calcium metal and tin. Calcium aluminum alloys are produced using Cal-Grid™ alloys produced by Minteq International, and soft lead. The final metal, when in specification, is pumped to a Wirtz casting machine and cast into 68 pound ingots.

Antimonial lead alloys are manufactured from blast furnace bullion remelted in a designated refinery kettle. Reducer is added to remove any residual oxides or sulfides. If required, copper is removed with sulfur. The levels of antimony, arsenic, and tin are then adjusted by the additions of pure metal or alloys, and the kettle is washed with sodium hydroxide followed by a charcoal treatment. Finally sulfur is added to specification. The alloy, when in specification, is cast on the Wirtz casting machine into 68 pound ingots.

Waste Water Treatment

Waste water treatment is done through a centralized facility where waste water from all of the campus manufacturing facilities is processed. In 1996 a new process was started to virtually eliminate discharge and to provide treated water for use in all the facilities. This process was described by Wolfe, Suenkonis, & Dellicker in 1998.[7] It combines traditional neutralization, and iron co-precipitation with reverse osmosis (RO) and an evaporator/crystallizer for the production of sodium sulfate.

Both the evaporative cooling requirements and the production of NS solution from the off gas scrubbing, cause the smelter to be a water consumer. Treated water from waste water treatment is used in the scrubbing process and RO reject is used for evaporative cooling. Iron sludge from the treatment plant is returned to the cupola feed to recover heavy metals and to utilize the iron in slag formation.

NESHAP & Ambient Air Quality

The 1990 Clean Air Act Amendments revised Section 112 to first require issuance of technology-based standards for major sources and certain area sources. For major sources, Section 112 requires that EPA establish emission standards that require the maximum degree of reduction in emissions of hazardous air pollutants. These emission standards are commonly referred to as "maximum achievable control technology" or "MACT" standards. Secondary Lead smelters must demonstrate compliance with 40 CFR Part 63, Subpart X - National Emission Standards for Hazardous Air Pollutants from Secondary Lead Smelting.

In addition to stack sampling requirements there are a number of performance standards within the NESHAP standard for the operation of baghouses, leak detection, total enclosure and maintenance of negative pressure on the operation, and control of fugitive emissions from storage areas, plant roadways, and material transport. While EPM has always followed a program of enclosure, isolation, and ventilation, these requirements have lead EPM to utilize not only PTFE membrane bags in its baghouse operations, but to also follow the baghouses in series with HEPA filtration. Both the pressure drop across the systems and the fan amperages are monitored to demonstrate compliance.

Stack testing is required annually to demonstrate compliance with 40 CFR Part 63, Subpart X. All air pollution control devices in the smelter both process and ventilation are required to be tested. Results for 2016 are as presented in Table 1.

Table 1. Stack Sampling Results June 2016 - Smelter
EPA standard 0.000087 gr/dscf

APC Number	Description	Gr./DSCF	ACFM Volume
BH 1	MSB ventilation	0.000001	66,145
BH3	Blast furnace hygiene ventilation	0.000003	30,286
BH4	Refinery	0.000004	27,287
BH5	Furnace process gases	0.000002	35,668
BH5A	Reverb furnace hygiene ventilation	0.000003	28,347
BH6	Rotary dryer ventilation	0.000007	12,166
BH7	Slag storage building	0.000001	77,081
SBB	Battery breaker scrubber	0.000063	34,722

Under the National Ambient Air Quality Standards, lead in ambient air is set at a standard of 0.15 µg/M^3 based upon a three month rolling average. The State of Pennsylvania operates two high volume air sampling stations adjacent to the manufacturing campus. At both of these locations EPM has a co-located monitor. Results from EPM's monitoring are as shown in Table 2. These results represent the performance of the whole complex not just the secondary lead smelter.

Table 2. Ambient High Volume Air Sampling Results µg/M^3 EPA Standard 0.15 µg/M3		
Year	**Lyons Borough Hall**	**Lyons Fire Company**
2012	0.052	0.050
2013	0.029	0.019
2014	0.022	0.016
2015	0.021	0.015
2016	0.020	0.017

Personnel Exposures

Personnel exposures are measured through individual personal monitoring of job tasks and by personal blood lead samples conducted monthly. Emphasis is placed upon proper hygiene techniques to minimize the potential for inhalation or ingestion of lead. Through the BCI and the ILA there has been a voluntary effort to lower the medical removal level to 30 µg/dl from the OSHA requirement of 40 µg/dl beginning January of 2017. EPM is participating in this effort. Average results of smelter personnel on an annual basis are shown in Table 3.

Table 3. Personnel Blood Lead Average µg/dl whole blood OSHA Standard: 40 µg/dl Voluntary Standard (2016): 32 µg/dl		
Year	**Smelter Average**	**95% UCI**
2012	18.2	28.3
2013	18.5	31.3
2014	17.6	31.2
2015	18.0	28.6
2016	17.1	30.2

Table 4 provides information on the personnel exposures by job type within the smelter. A great deal of emphasis is placed upon good housekeeping, proper work techniques, proper utilization of the ventilation, isolation from potential exposures, and prevention of fugitive emissions within the work area. Tasks which are known to have potentially high exposures are done with specific operating procedures and with specialized personal protective equipment.

Table 4. Personnel Lead Exposures µg/M^3 OSHA Standard: PEL 50 µg/M3			
Job Function	**2016 average**	**Job Function**	**2016 average**
Supervisory	25	Battery Breaking	39
Furnace	47	Front end loader	81
Refinery	55		
Casting	26	Acid reclaim	1
Clean up	27	Plastic Reclaim	9
Scrubber	20		
Maintenance	22		

Summary

The secondary lead smelter at East Penn Manufacturing Co., Inc. is an integral part of the vertical integration of the Lyons manufacturing campus, providing raw materials for the battery manufacturing process, but also integral to the sustainability and product stewardship of lead-acid batteries through the cradle to cradle approach. The operations are complex, capital intensive, and driven by environmental compliance and personnel exposures to toxic materials. Through the cradle to cradle approach, lead-acid batteries remain one of the highest recycled consumer materials in our society.

List of Works Cited

The following are references cited within the paper:

1. K.N. Pike, "Secondary Lead Blast Furnace Smelting at East Penn Manufacturing Co., Inc.", Lead-Zinc '90, T.S. Mackey and R. D. Prengeman, Eds. TMS, Warrendale, PA, USA, 1990, pps. 955-969.
2. R. A. Leiby Jr., "Secondary Lead Smelting at East Penn Manufacturing", 1993 EPD Congress, J. P. Hager, Ed. TMS Warrendale, PA USA, 1992, pps. 943-958.
3. R.A. Leiby Jr., "Secondary Lead Smelting at East Penn Manufacturing Co., Inc. Changes Since 1993", Lead & Zinc '05, Vol I, T. Fugisawa, Ed., MMIJ, Kyoto, Japan, 2005 pps. 601-613.
4. R. Leiby, M. Bricker, and R. Spitz, "The East Penn Manufacturing Process for Recycling Sulfuric Acid from Lead Acid Batteries", 3rd International Symposium on the recycling of metals and Engineered Materials, P.B. Queneau and R. D. Peterson , Eds., TMS, Warrendale, PA, USA, 1995, pps. 311-319.
5. R. Leiby, M. Bricker, and R. Spitz, " The Role of Electrochemistry at East Penn Manufacturing Co., Inc.", 4th International Symposium on the Recycling of Metals and Engineered Materials, D. L. Stewart, R. Stephens, and J.C. Daley, Eds., TMS, Warrendale, PA, USA, 2000, pps. 141-151.
6. R. D. Prengeman, "Reverberatory Furnace – Blast Furnace Smelting of Battery Scrap at RSR", Lead-Zinc-Tin '80, J.M Cigan, T.S. Mackey, and T.J. O'Keefe, Eds., TMS of AIME, Warrendale, PA 1980, pps. 985-1002.
7. D. Wolfe, C. Suenkonis, and D. Dellicker, "Combining Treatment Technologies to Eliminate Wastewater Discharge", Pollution Engineering, August, 1998, pps. 38-40.