



General Industrial Issues

Sound Management of Solid Waste in the Lead Industry

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Solid wastes in the lead industry are potentially hazardous and can represent a serious threat to human health and the environment. The Lead Industry bears a special responsibility to ensure that both primary and secondary processes are Environmentally Sound and that the risks to occupational health, population exposure and environmental contamination are minimal.

1. Sources of Solid Waste

The largest amount of solid waste produced is in mining operations. As the metal content of mined material is very small it is hardly surprising that huge quantities of rock and tailings are produced every day. Secondary lead recycling plants generate waste from, for example, recovered vehicle battery cases and furnace residues.

Mining, primary smelting, secondary recycling plants and applications industries all produce lead by-products. Spillage, particularly in the form of fine dusts, can present a serious hazard to successful waste management. Furnace and casting refractories have to be replaced periodically and are classified as a hazardous waste because they are invariably contaminated with metallic residues.

Operating tools, for example dressing spoons and equipment such as baghouse filter bags require special consideration prior to disposal. At some sites the operating plant and equipment lubricants will also be contaminated by the process and represent another source of hazardous waste.

Packaging, such as chemical reagent bags and wooden pallets, used to transport vehicle batteries to a recycler, produce large volumes of waste that can be contaminated.

2. Solid Waste Properties

The various solid wastes generated by the lead industry vary considerably in their chemical and physical properties. Waste can be soluble, such as sodium based refining drosses and insoluble, such as blast furnace slag.

Packaging will be lightweight whereas discard slag will be dense and heavy. Furnace fume can be dusty whereas blast furnace slags are often granulated, but can be bulky in the form of unbroken or partly broken "buttons".

Most of the waste is mineral based and inorganic, but some of the materials, such as wooden pallets and used battery cases, are organic.

Depending on the nature of the process some intermediate stages will produce acidic by-products and others generate alkaline by-products. Whilst these by-products are not for disposal they will, in certain circumstances, leave one site for further processing at another.

Certain waste materials are potentially toxic, for example certain arsenical residues, while others, such as silica based slags, are essentially inert.



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3. Causes of Potential Risks

Certain furnace residues, particularly those associated with caustic softener skim and soda ash flux, produce lead salts that are partly soluble, bio-toxic and have the potential to weather, degrade and leach into the environment.

Failure to capture and contain by-product dusts and furnace fume can quickly result in occupational, population and environmental exposure.

Unnecessary exposure can also be caused by inadequate materials handling during processing, uncovered transportation and storage of these wastes on open ground or uncovered bays.

Certain lead contaminated wastes and by-products are not economic to recycle and once rendered inert are legally disposed of at landfill sites.

Nevertheless, it is becoming increasingly clear that the legal landfill disposal of lead contaminated waste today is likely to be unacceptable in the near future as a method of Environmentally Sound Management.

4. Analysis of Solid Waste

Solid waste testing is essential to monitor performance, but it is also important to conduct a physical inspection of any solid waste to ensure that the waste is metal free.

Solid waste must be analyzed and tested for lead content and the presence of other heavy and toxic metals such as arsenic and cadmium. The toxicity characteristic of any slag waste should be determined using the standard Toxic Characteristic Leaching Procedure (TCLP).

Analyzing furnace residues for fluxing agents such as iron and silica is an extremely useful energy saving tool because it will assist in optimizing the flux additions and minimize smelting temperatures according to the appropriate phase diagrams.

Test for soluble sodium salts in white slag prior to disposal or leaching.

Any materials recovered for recycling, such as polypropylene should be sampled and tested for lead residues. Again a visual inspection during the processing stages of the operation is important to ensure adequate washing.



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5. Control of Solid Waste

From the lead mine to final product manufacture efficient processing of materials to minimize the formation of by-products and discard residues is one of the most important factors in the management of solid waste.

It is essential that appropriate engineering solutions are applied to ensure that solid waste, particularly fine dusts and soluble material is captured and contained prior to either reprocessing or disposal.

Good housekeeping in the workplace and around the waste storage areas is vital to reduce the risk of occupational and environmental exposure.

Wherever possible every effort should be made to either recycle or find a practical application for any solid waste material and where this is not feasible seek an internal method of disposal.

Ideally the industry should be operating so that the absolute minimum amount of solid waste requires "off site" disposal.

6. Efficient Processing

As the process, represented by the area with the dots in the triangle, proceeds solid waste, represented by the black balls area is generated.

All too often companies try resolving their waste management problems by treating the waste after it has been generated. This approach is an "end of pipe" solution.

However, the most effective reductions in re-circulating by-products and waste residues require an integrated approach and an analysis of the whole process.

In recent years many of the major primary and secondary lead producers in the United States have reduced their overall solid waste and by-product burden by as much as 80% by "attacking" the management of waste at the various processing phases.

Intermediate wastes, that is, by-products, represent a significant occupational and environmental risk if not managed properly and whilst their containment and handling are dealt with later it is worth noting that efficient processing will again reduce the by-product burden.

A simple example would be the charging of red hot molten furnace metal to a refining kettle. Charged from some height above the lead bath in the kettle and at smelting temperature produces considerably more dross than either tapping the molten metal from the furnace to blocks, and then melting the blocks in a refining kettle, or tapping the furnace hot metal directly to a molten lead bath.

Another example would be the two stage double processing of certain refining reagents, such as caustic soda in kettle softening in order to reduce the amount of by-products that need to be reprocessed.



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There are many examples, but one of the best can be found at the Cominco Lead and Zinc Smelter.

6.1 Cominco Slag Treatment

At the Cominco Lead and Zinc Smelter in British Columbia, Canada, the metallic slag, containing all of the iron and most of the zinc from the Kivcet Furnace, is transferred in 70 t batches to a coal-fired fuming furnace. To recover the zinc, fine coal and air are injected one metre below the top of the slag bath. Initially the coal reduces the zinc oxide in the slag to metallic zinc. Metallic slag, containing all of the iron and most of the zinc from the Kivcet Furnace, is transferred in 70 t batches to a coal-fired fuming furnace. To recover the zinc, fine coal and air are injected one metre below the top of the slag bath. Initially the coal reduces the zinc oxide in the slag to metallic zinc. The heat generated then vaporizes the zinc and as it rises from the furnace bath it is immediately re-oxidized by tertiary air to form zinc oxide fume. This fume and the hot gases are cooled in a waste heat boiler before passing through a baghouse to collect the zinc fume for treatment in the adjacent Fume Leach Plant. Here the halogens (chlorine and fluorine) are removed by a sodium bicarbonate treatment. The exhaust and ventilation gases from this entire process are discharged to a tall stack. The molten barren slag is granulated in water then collected for sale to cement manufacturers.

Cominco are currently supplying barren slag to the Portland cement industry. The barren slag supplies iron to the raw material mix for the cement. Whilst the barren slag is sold for this purpose it is a low value material and any potential profit is offset by the freight charges. However, over the past 8 years Cominco have developed a value added product in conjunction with Pildysh Engineering. The product consists of Cominco finely ground barren slag (D50 of 8 to 10microns) and a proprietary additive. Currently Cominco are marketing this product for about 70%to 80% of the Portland cement price.

The pilot plant now operating (2001) has only a limited production capacity, but Cominco are planning to build a 30,000 metric tons per year permanent facility that should go into production early in 2002.

7. Capture and Containment

The most environmentally friendly lead processing plants in the world today are completely enclosed or encapsulated. This might not be an economic option for many companies, but the principle can be applied to each stage of processing so that, for example, all furnaces are hooded and refining kettles covered to ensure that by-products are contained.

Lead fume and vapor producing processes must also be ventilated to baghouses for collection and reprocessing.

By-products are often difficult to handle and it is very important to minimize occupational exposure and ensure that all collection vessels and skips are sealed. Transportation of any dusty material, whether for reprocessing or disposal should be by either closed conveyor or pneumatic transfer lines.



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By-products, intermediate recycled materials such as battery case polypropylene and disposable waste should always be stored under cover to reduce the risk of any unforeseen exposure.

8. Good Housekeeping

One of the most effective methods of reducing occupational exposure, especially that associated with by-product dusts is to maintain high standards of housekeeping.

All work areas should be cleaned daily with either a portable, a mobile or fixed Vacuum cleaning equipment. Mechanical sweepers or brooms, which are notorious for generating dust clouds, should never be used.

Any spillage should be cleared away immediately to avoid the risk of airborne contamination.

Site roadways, including those approaching the plant, should be damped down and cleaned so that rainwater is not contaminated with leaded materials. All vehicles that leave the site should be washed down with either high-pressure water sprays or pass over a "rumble" bath which washes the wheels and also shakes free any material sticking to the tires. All wheel wash effluent must be drained to a settlement lagoon so that the water can be filtered, to remove solid particles prior to re-circulation.

To reduce the risk of exposure in works offices and canteens "tack" mats should be used at every entrance to effectively remove loose dust from shoes and boots. The top section of the mat is periodically peeled away to reveal another "tacky" section and the contaminated sheet sent to the furnace for processing.

9. Effective Utilization

One of the most classic cases of effective utilization of waste material can be found in the lead mining industry where vast quantities of ore are removed from the lead bearing stopes for processing. The waste rock is not, however, dumped, but is an integral part of the mining process.

Irrespective of the method of mining a lead bearing stope the waste material is used to provide a working surface and often support for the stope walls. Indeed in certain mines the utilization of this waste material has extended the economic life of the ore-body.

Secondary lead smelting companies are already expert in the recycling of battery case polypropylene and it is important to extend this concept to other waste materials such as inert furnace slags, which if granulated (preferably during the tapping phase of the process) have the potential to be an excellent hard core for road building.

By-product re-circulation is an expensive part of any operation and can be reduced by process changes, although this will often require the installation of a new furnace. Alternatives include bricketting and feed mixing to ensure adequate smelting of the by-products and minimum re-circulation.



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A very good example can be found at the Doe Run Battery Recycling Plant in Buick, Missouri, USA.

9.1 Dust and Fume Furnace

Leaded dust, in particular baghouse fume, is a very difficult by-product to treat. All the major lead smelters return this by-product to the process for recovery, but because the "residence" time for these fine dusts is so short, even when mixed with the recyclable feed material, much of the dust and fume returns to the baghouse untreated.

At the Doe Run Battery Recycling Plant at Buick, Missouri, the process can produce up to 80 tons of dust and fume a day. This dust is collected in a baghouse and then conveyed, via a storage silo to a specially designed refractory lined dust agglomeration furnace.

This dust fume furnace has two oxygen enriched propane fired High Ram burners. One burner is located in the roof, aimed directly at the feed pile and the other is located in the end wall aimed directly at the feed pile.

The furnace chamber gas temperature is maintained between 980°C and 1200°C, depending on the metallurgical components of the baghouse dust. The gas outlet duct from the furnace is refractory lined and is mounted in the center of the roof. This outlet duct is sloped at 60° to the process gas cooling chamber, where it commingles with other process gases prior to the baghouse. The agglomerated slag is cast into a solid tapered 360 kilo block and then reduced in size prior to re-processing through the Buick Blast furnace. The furnace "residence" time of the rock hard agglomerated leaded fume and dust is substantially increased and most of the lead is recovered with a pro-rata reduction in the re-circulating by-product load.

10. Minimal Disposal

Effective integrated production management of atmospheric, liquid and solid waste will minimize the amount of re-circulating by-products and discard waste produced in the process and increase the possibilities for recycling materials.

If an integrated waste management solution requires a process that is not available on a particular site or in one company, it is incumbent on the industry to cooperate and assist each other to identify a plant that could reprocess the lead bearing material. Such arrangements are not unknown and can be profitable. This form of cooperation is particularly suited to small and medium sized operations where investment in by-product treatments can be uneconomic. Accordingly such arrangements should be encouraged as a further enhancement to Environmentally Sound Management.

Consideration should also be given to reducing the risk of lead exposure from waste that cannot be recycled. In this instance an example might be the disposal of lead contaminated refractories. It is difficult to remove the lead contamination without some risk of occupational exposure.



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However, those sites with either an oxygen blast or cupola furnace could, subject to local hazardous waste disposal regimes, smelt the used refractory bricks together with the charge material, recover the lead and render the refractory material harmless as part of the inert slag.

Certain other drosses and slags may need leaching to remove lead contamination and with tighter legislation in some countries, solvent extraction is now being seriously considered as the most appropriate option.

11. What Is "Green" Technology?

Certainly, there are Lead Industry residues classified as "hazardous" and are potentially polluting. Increasingly, however, the industry is producing "inert" slags, either directly or indirectly, that are non hazardous and can be considered as a product of a "clean" technology.

Nevertheless, both hazardous and inert residues are solid wastes and require landfill. Dumping solid waste to landfill, even non hazardous wastes, is not sustainable and therefore cannot be regarded as "green".

Ideally, a "green" technology is one that consumes all materials involved in the production process to produce only re-useable or new saleable products without generating any solid waste that requires disposal to landfill, as already demonstrated at the Cominco Plant in Canada.

So let us look at some more examples of where the lead industry has introduced successful "clean" and "green" technologies to address solid waste management issues.

The first example is the "Green Slag" Process that successfully converts a secondary smelter from being a producer of hazardous waste to producing an inert and "clean" residue. The second example will demonstrate how the concept of the "Green Technology", producing only saleable "clean" products and no waste, can be fulfilled through the PLACID Process for recycling used lead acid batteries.

11.1 "Green slag" Process

Rotary Furnaces are commonly used around the world for the recovery of lead from secondary materials, such as used lead acid batteries. In many cases operators are using sodium based fluxes and producing unstable and leachable lead bearing slags.

These "white" slags are expensive to dispose of in properly managed licensed landfills and where there are no suitable toxic waste dumps, for example in the Philippines, the residues could represent a serious threat to the environment.

Over the past 5 years the Mexican based Lead Metal Technologies has developed and improved the rotary furnace smelting of secondary lead materials to achieve the production of a non-hazardous "Green Slag" complying with the stringent USA EPA TCLP standards.



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In order to produce a "green slag" existing Rotary Furnaces will need to be re-engineered with specialized auxiliary equipment and the smelting process controlled by a specially written Lead Metals Technologies software program, in conjunction with carefully blended and precise charge materials, including refinery by products and baghouse fume. (Typically 5 different charge mixes)

The process has been successfully commissioned at leading secondary Lead recycling operations in Canada, Mexico, Venezuela and Brazil.

11.2 The Técnicas Reunidas PLACID Process

Advances in hydrometallurgical technology for the recycling of used lead acid batteries promoted by, in particular, the Spanish Company Técnicas Reunidas, are providing increasingly simple and clean processes.

Essentially following from conventional battery breaking, the paste is leached in dilute hydrochloric acid in brine solution to dissolve the lead oxides and sulphates. The sulphate contamination is removed with lime in a carefully controlled manner to precipitate a commercial form of Gypsum, which is then removed by filtration.

Lead powder is then injected into the leachate to precipitate the metallic impurities such as Cu, Bi, Sn, Ag, As, Sb and so on.

The electrolyte for the two electrodes in the PLACID electrolytic cell are different, and separated by a membrane that is permeable only to proton ions (H⁺). On the cathode, lead chloride is stripped of its lead atom, leaving two negatively charged chloride atoms, which in turn combine with protons passing through the membrane from the anode to reform hydrochloric acid, which is returned to the leaching bath for reuse. The electrolysis deposits lead as dendrites (spongy form of lead). The dendrites are shaken off, collected and removed from the bath on a semi-submersed conveyor belt. The dendrites are pressed to expel excess electrolyte to form platelets of pure lead that can be melted in a conventional refining kettle and cast into ingots of 99.99% pure lead.

11.3 Environmental Benefits of the Técnicas Reunidas PLACID Process

The Environmental benefits of the PLACID hydrometallurgical process are:

- a. There are no liquid effluent discharges and the hydrochloric acid used in the initial leaching process is regenerated.
- b. The process produces half the amount of solid residues compared to conventional pyro-metallurgical recycling and the residue is a saleable commercial grade Gypsum.
- c. There are no sulfurous or greenhouse gas emissions from the plant.
- d. Any dust or drosses collected during the recycling process can be recycled through the leaching process.



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- e Lead contaminated slags from pyro-metallurgical recovery operations and contaminated soils from abandoned mine sites and disused lead smelters can be treated using the PLACID process and the lead content removed.

12. Waste Management Solutions

There are essentially seven stages to effective Waste Management Solutions:

1. Adopt a Waste Management policy endorsed by the most senior executive containing the principles of sustainable development and lead risk reduction.
2. Integrated operating processes to maximize the recovery of lead and other valuable metals, minimize re-circulation of by-products, provide for the segregation of materials that can be recycled and produce the minimum amount of disposable waste.
3. Comply with International (Basel Convention) and National Environmental and Health performance standards for solid waste management.
4. Ensure that the relevant supervisors and line managers and any personnel under their direction are familiar with the strict requirements for hazardous waste disposal and abide by company procedures and regulations.
5. Any personnel involved in the generation of waste, especially hazardous material, should ensure that it is collected in a suitable container, labeled and subsequently stored safely pending recycling or collection for final disposal.
6. Demonstrate adherence to Environmental and Health performance standards through accredited audit procedures such as the ISO 14000 series.
7. Communicate the essential reasons for and requirements of sound environmental management to the workforce, the local community and regulators through regular public briefings, updating operational performance and achievements.