BATTERY RECYCLING THROUGH BRITANNIA ZINC'S ISF PROCESS

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Abstract

Britannia Zinc owns and operates a zinc smelting and refining operation at Avonmouth near Bristol in the UK. The plant, which produces around 100,000 tonnes of refined zinc per annum, employs the Imperial Smelting Process. This process consists of a number of discrete steps in the path to recovery of valuable metal. A particular feature of Britannia Zinc's plant is its ability to treat a wide range of feed materials with variable specifications. A further feature is the ability to effectively deal with a range of potentially environmentally harmful substances, including mercury, cadmium, lead and sulphur. Within the minerals and metals industries, there has been a growing appreciation of the contribution that can be made towards worldwide sustainable development efforts. Increasingly, this is being recognised by government bodies and the wider community. In line with this, Britannia Zinc is looking to increase the contribution it makes towards the development of innovative and sustainable means by which the waste arisings of modern society are managed. As part of these efforts, Britannia Zinc has been examining the processing of spent portable batteries through its plant. This project has been undertaken with the support of the local government authority, the regional development agency and the UK government authority responsible for trade and industry. This paper presents details of the project to date.

Introduction

Britannia Zinc Limited (BZL), is wholly owned by MIM Holdings, an Australian-based international mining and metals company. The production of marketable grades of zinc, lead and silver through a number of operations worldwide represents a major business stream.
BZL is located in Avonmouth, north west of the city of Bristol, near the Severn Estuary and the port of Avonmouth. Smelting operations began at Avonmouth in the late 1920's. Technology used on site has progressed from the early Horizontal Retort (HR) and Vertical Retort (VR) processes to the development of the 'Imperial Smelting Process' (ISP). Following its operation at pilot scale, the ISP was licensed worldwide and is now a major contributor to world zinc and lead production. The plant in current use was built at Avonmouth in 1967/68, and has been progressively upgraded and improved, in many cases to enhance environmental performance.

Process Operations

Raw Materials

Around 300,000 tonnes per annum of raw materials are treated by BZL. At present, mine concentrates comprise the majority of feed materials, though throughputs of secondary materials, which have been processed for a number of years by BZL, are increasing. In the 12 months to June 2003, 80,000 tonnes are scheduled, including zinc scrap, zinc-rich dusts and residues from steel recycling plants, and residues from metals production and galvanising plants.

Mine concentrates and some other raw materials are received at Avonmouth Docks and transferred by conveyor to enclosed storage bunkers. Other materials are delivered by road, including most secondary materials and ancillary materials such as fluxes and coke. Secondary materials in dust form are fed directly into silo storage.

A number of internally recycled materials are also required to be handled, stored and sometimes pre-treated before being re-processed.

Sinter Plant

The sinter plant (Figure 1) converts feed materials to a suitable physical and chemical form for blast furnace extraction of metals. In the process, mixed feed materials are de-sulphurised and agglomerated into large lump form.

Concentrates, recycled sinter fines and other process materials are proportioned, conditioned and blended before being fed to the sinter machine. This material is then ignited and roasted, air is blown through and the mix is oxidised.

The gas stream from the process contains about 6% sulphur dioxide, and is directed to the sulphuric acid plant. Sintered material is separated into two streams, being suitably sized lumps for forward feed to the ISF, and fines which are recycled to sinter feed.

Sulphuric Acid and Cadmium Recovery Plants

The purpose of these plants (Figure 1) is to recover the sulphur contained in the gases from the sinter plant as sulphuric acid, and to extract cadmium from the solids in the gases for transfer to the refinery.

Firstly, dust-containing gases are cooled and cleaned by wet scrubbing, packed tower cooling and electrostatic precipitation. Mercury is then removed by scrubbing with mercuric chloride solution, and the gases dried by contact with sulphuric acid. The clean, dry gas then passes to a converter, where sulphur dioxide is oxidised to sulphur trioxide and then recovered by absorption in sulphuric acid. The plant is of single-contact design, and up to 98.5% conversion of sulphur dioxide to acid is obtained.

Sulphuric acid produced is commonly bleached using hydrogen peroxide to give a white acid product, which is marketed for various industrial uses.

In the cadmium removal plant, a bleed of sinter gas scrubbing liquors are treated in a series of steps to produce crude cadmium metal sponge, as well as recyclable sludge. Cadmium sponge is heated with caustic soda and cast into ingots in preparation for refining.

Imperial Smelting Furnace (ISF)

The ISF (Figure 2) simultaneously extracts zinc and lead from sintered concentrates and other feedstocks, including direct-fed secondary materials. It is a modified blast furnace in which preheated air is injected into a mix of top fed metal feedstocks and coke held at about 1000°C. Carbon from the coke is converted to carbon monoxide which reduces zinc and lead oxides to their elements.

In the ISF, zinc is vapourised and leaves the furnace top for rapid cooling in lead splash condensers. In these, the zinc is collected and continuously separated by cooling, then tapped into ladles. Any cadmium present accompanies the zinc. Residual gas containing 20-25% carbon monoxide also leaves the furnace top, and has a low but useable calorific value. It is cleaned and cooled and a high proportion is burnt to preheat blast air and coke.

The non-volatile components of the feed pass down the furnace shaft and are tapped off as lead bullion containing dissolved gold, silver, copper and antimony, and slag containing iron oxides, silica, lime, alumina and arsenic. The lead bullion is cast into blocks and sent for refining off site. The molten slag is granulated and quenched using recirculated water and is then transferred to a licensed on-site landfill.

Some finely powdered materials (both internal recyclables and imported dusts) can be directly injected through tuyeres into the ISF shaft for additional metal recovery.

Zinc and Cadmium Refinery

The refinery (Figure 3) purifies crude zinc and cadmium into saleable products. Feeds include crude zinc from the ISF and cadmium ingots from the caustic cadmium furnace. A series of pyrometallurgical and chemical steps are employed to separate zinc and cadmium and remove impurities such as lead and arsenic.

Battery Processing

With the implementation of the EU Battery Directive, it is possible that around 10,000 tonnes of batteries could eventually become available for recycling in the UK, when collection systems are in place and operating efficiently.

As previously noted, the Avonmouth plant is already treating recycled materials from the zinc and steel making industries, and appears capable of handling additional waste materials, including used portable batteries. Technical work carried out to date indicates that the plant is able to treat unsorted mixes of batteries collected for recycling.

Batteries would be received on site and either discharged into existing covered storage bunkers, or stored in enclosed containers. It is intended that they would be blended in optimum mixes with other primary and secondary feedstocks, and furnace additives. They would then be fed directly to the furnace through the sealed double bell charging system utilising equipment and procedures currently used for lumpy, metallic recycle materials.

As a large metallurgical plant treating and processing a wide range of metal bearing feed materials, including lead and cadmium, BZL has comprehensive health and safety procedures in place for the protection of employees. These systems are believed to be compatible with requirements for battery recycling. All battery handling will be mechanised, with suitable protective clothing worn by operators involved in the recycling operation as appropriate.

Once inside the furnace top, the batteries are expected to break open and mix with other charge components. For commonly treated battery types, including alkaline manganese, zinc carbon, nickel cadmium and zinc air, the battery contents will react in the same way as normal charge materials in the reducing conditions present in the blast furnace, as follows:

- Zinc metal will melt and volatilise to zinc vapour and will pass though the off-take to be recovered as zinc metal in the lead-splash condenser process.

- Steel in battery casings will act as a reductant for zinc oxides and will then enter the blast furnace slag as iron oxide. Carbon, together with plastics and paper casings which will be oxidised to carbon monoxide, will act as a chemical reductant for metal oxides.

- The manganese dioxide paste will enter the slag phase. Zinc chloride paste will be thermally decomposed and enter the gas stream as zinc vapour and chlorine. The zinc will then be recovered in the lead splash condenser as product, while chlorine will eventually exit the site in treated effluent, after scrubbing the off-gases with water.

- Cadmium will be volatilised and will pass with the zinc to the zinc refinery for cadmium recovery as product.

- Mercury will volatilise in the furnace and be removed from the off-gases in the lead splash condenser and the gas scrubbing plant, into so-called 'blue powder' slurry for recycle to the sinter plant. In the sinter/sulphuric acid plant the mercury will be converted to calomel (mercurous chloride) in the mercury recovery process. Calomel is presently sent to a licensed chemical waste site. A small amount of mercury may condense with furnace zinc in the lead splash condenser and carry through to the cadmium product.

- Nickel will report to slag and to the crude lead product. During lead refining the nickel will enter the copper-rich drosses for further downstream processing

- Silver will be recovered in the crude lead product from the furnace bottom and sent to a lead refinery for eventual recovery as refined silver.

It is expected that other battery types will be present in the mix for recycling in relatively minor amounts. Some of these are discussed briefly as follows:

- Nickel metal hydride rechargeable batteries contain oxides and hydroxides of nickel and cobalt which will be distributed to slag and crude lead product, as well as alkaline hydroxides of lithium, sodium and potassium which will go into slag. Also present are rare earth elements lanthanum, cerium, neodymium and praseodymium which will behave similarly to iron and pass into the slag.

- Lithium-iron bisulphide and lithium ion (rechargeable) batteries contain significant amounts of organic and metallo-organic compounds. These are expected to combust fully in the furnace with the lithium oxide entering slag. Combustion products will include carbon dioxide, hydrogen, nitrogen or nitrogen oxides, fluorine and chlorine. These will either exit in exhaust gas or be scrubbed in the gas cleaning system and leave the process in effluent, both in undetectable amounts. Any propensity to form dioxin type compounds in this gas mix is prevented by the rapid cooling process of the lead splash condenser in which gases shock cool from 1100C to less than 600C almost instantaneously in an intense shower of molten lead. As a part of its environmental licence (Integrated Pollution Control), BZL has in place a ‘Secondary Materials Protocol’ which requires routine confirmation by emissions testing of dioxin destruction in the ISF.

- Non-spillable lead acid batteries will behave in the same way as similar lead materials already handled in the process.

Processing of batteries is anticipated to have a negligible impact on emissions to air and water. Main points include:

- Material handling operations from reception at site to loading into ISF charge bells will result in negligible airborne emissions with the batteries in their original, or nearly original, physical forms.

- In the furnace operations, the primary exit route for emissions to air is the Low Calorific Value (LCV) process gas stream, which is cleaned by two modern Theisen disintegrators. At likely shaft feed rates of batteries to the blast furnace, the replacement of sinter feed by batteries will have no discernible impact on LCV furnace tail gas emissions compared to current performance.

- No measurable increases in emissions at other parts of the process are expected from the slight changes in drosses or blue powder recycled back through the ISF or sinter plant.

Proposed Processing Trial

A trial batch of 100 tonnes is proposed to confirm the BZL furnace processing option and its potential capacity for portable batteries. The trial will also be used to confirm assumptions about recovery levels of zinc and cadmium, and the dispersement of other elements to products, by-products and controlled emissions. During the trial, feed rates of batteries will be varied to simulate probable ‘steady state’ feed rates, as well as maximum short-term rates that can be reasonably foreseen.

Routine stack testing of the ISF and Sinter Plant discharge stacks would be scheduled to coincide with the trial. Results would be analysed in relation to results currently achieved.

Slag in Construction Project

BZL produces a significant amount of slag as a process by-product, which is presently deposited to an on-site landfill. In line with the likely requirements of the Battery Directive, BZL is working towards the successful demonstration of an end use for this slag.

Efforts in actively exploring potential outlets for slag have been ongoing for a number of years, and have centered around its potential in construction applications. The demonstration of engineering and environmental credentials has been recognised as key to the success of these efforts. To this end, BZL has actively supported and participated in a number of relevant research projects.

Initial research had as its focus characterisation of the chemical and physical properties of the slag, together with 'desk-top' analyses of its potential in various applications. Physically, the slag by nature is sand-like, granulated material. Research efforts have progressed to the point where the most promising applications appear to be in bound form in concrete and bitumen. A new research project, entitled 'Use of Non-Ferrous Waste Streams as Bound Aggregates in Waste Streams' was commenced in January this year. This project, which has as its focus wastes produced by the aluminium, zinc and lead industries, including BZL slag, is being coordinated by Building Research Establishment, a large, private UK organisation which specialises in building and construction research. The project has a high level of government support, particularly from the Department of Trade and Industry, and from the Environmental Trust established to administer the UK Landfill Tax Credits scheme. The project has also the involvement of the Environment Agency, the Highways Agency, British Standards and leading UK concrete and bitumen companies.

The project has as a feature the establishment of demonstration projects, which are intended to provide a test for the slag in ‘real life’ situations, where laboratory-based research has indicated a strong likelihood of success. The first of these demonstration projects is planned for early July, when concrete roadway containing the slag will be laid. The performance of slag-containing roadway will be measured against control lengths of conventional concrete roadway.

The project, which is planned to run until mid 2004, represents a key plank in BZL’s efforts to gain acceptance for the slag in construction-based applications. These efforts are complementary to a number of emerging factors, including the introduction of an aggregates tax for newly quarried material, the implementation of the Landfill Directive, UK government efforts to promote sustainable construction, and the depletion of suitable natural resources for construction. BZL is confident of a successful outcome.

Bristol City Council Collection Trial

The BZL plant at Avonmouth is sited within the greater Bristol area. A Bristol-wide Pilot Battery Recycling Scheme is being set up to run for a 12 month period, commencing September 2002. The project partners include the South West of England Regional Development Agency (SWRDA), Bristol City Council (BCC), the Department of Trade and Industry (DTI), BCC’s recycling contractors, Sita and Resource Saver, and BZL. A Steering Group has been established to oversee the project, and a Project Manager is being recruited.

Collection systems for batteries during the trial are currently being planned. These will include kerbside collection, which will be incorporated into current systems, and bring sites, for which four existing sites will be enabled to receive batteries. The bring sites will have a good geographic spread across the Bristol area.

Depending upon results achieved when the scheme is launched, additional collection opportunities will be sought during the course of the trial, which may include school collections and supermarket bring schemes.

BZL will be the recipient of all batteries received. It is anticipated that processing of the Bristol batteries will follow the initial 100 tonne trial planned.

Support for the trial has been received from a number of bodies, including the project partners, and Sita's Environmental Trust established under the UK Landfill Tax Credit Scheme. The battery collection and recycling trial is seen by all participants as an extremely positive and exciting project with scope to generate significant interest and publicity, within the region as well as nationally. The initial priority is a 'call to action' locally, encouraging people to collect batteries for recycling, and educating them about how and why. A high profile multi-media campaign will be launched publicising the pilot, at both a regional and national level.

The project has a number of key aims, including:

- Assessment of the suitability of recycled batteries for introduction into BZL's production process;
- Collation of data on battery types, chemistries and volumes collected;
- Evaluation of the relative effectiveness of battery collection methods;
- Assessment of environmental impacts;
- Examination of infrastructure required to support battery recycling;
- Determination of costs involved in running the scheme;

- Assessment of the levels and continuity of public awareness and public response; and
- Researching of existing recycling schemes and markets throughout the world, and identification of best practice and potential pitfalls to avoid.

Following the completion of the pilot project, it is intended that a robust report be produced which covers all of the project's aims. The report will provide a case study to help the DTI, Local Authorities, Environment Organisations, Development Agencies and the private sector determine how the UK can best prepare for the impending issue of a European Directive on Battery Recycling.

Economics

From the treatment of batteries, BZL will recover zinc, lead and cadmium, for which established markets exist. Carbon present will supply some of the carbon reductant needed to process the batteries. As discussed in this paper, BZL is also working towards a sustainable, construction based application for slag produced, which would contain most of the balance of elements and compounds originally present in batteries.

Despite these recoveries, however, the battery treatment process will result in a considerable net cost to BZL. This is due to internal recycling requirements of intermediate products attributable to the batteries, process additions required for treatment and recovery steps, process energy requirements and various other costs associated with products, by-products and wastes. At present, these costs are yet to be determined, however a reasonable indication is likely to emerge in the near future with further technical analysis, together with the battery trials scheduled.

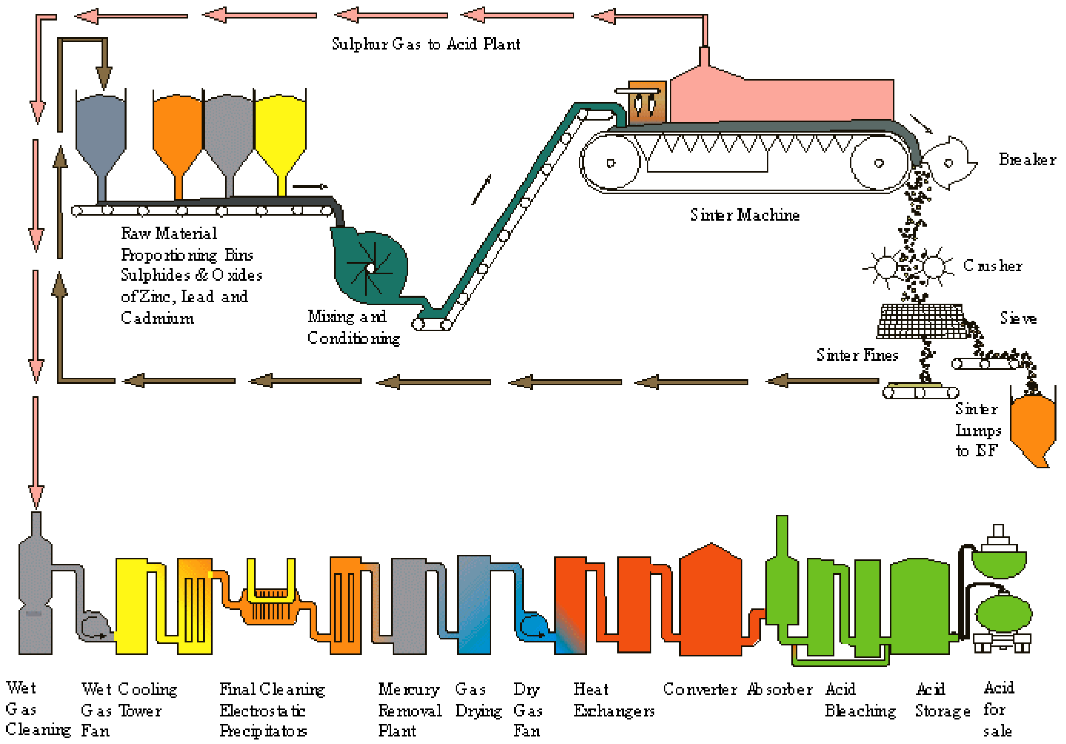

Figure 1: Sinter Plant Process Flow

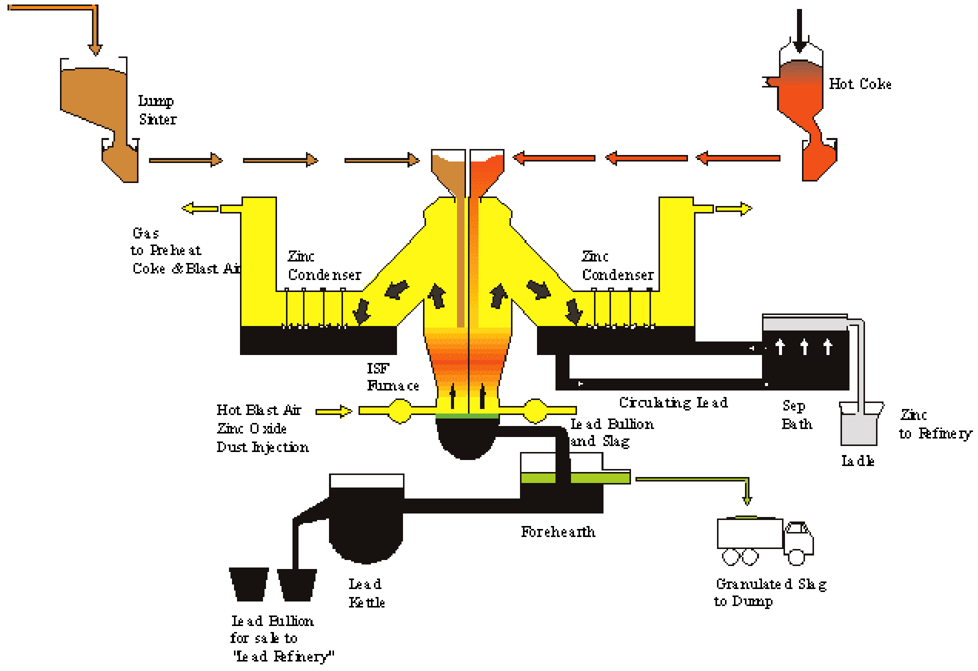

Figure 2: ISF Process Flow

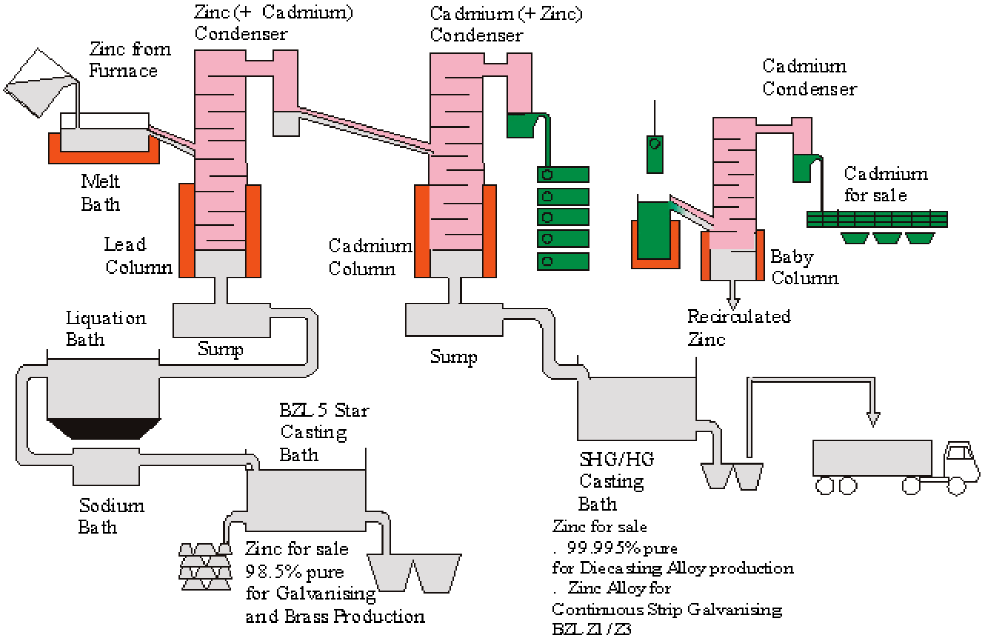

Figure 3: Refinery Process Flow