ISASMELT™ FOR LEAD RECYCLING

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ABSTRACT

ISASMELT™ is a well established technology for the smelting of primary copper and lead concentrates. Less well known is its application for the recycling of lead battery scrap. Two ISASMELT™ plants have been constructed to date for recycling lead batteries, producing a low-antimony soft lead plus a lead antimony slag from which a lead antimony alloy and a low-lead silicate slag can be produced. Sulphur capture has been achieved either by the use of a lime scrubber or by paste desulphurisation prior to smelting. The experience gained in these plants is extrapolated to a large scale (>300,000 tpa) plant.

INTRODUCTION

ISASMELT™ technology is now well established as one of the standard technologies for primary copper smelting [1]. There are currently seven primary copper plants in operation, with three further plants under construction. Three of the operating plants individually treat in excess of 1,000,000 tpa of copper concentrates, the maximum demonstrated throughput to date being approximately 1,400,000 tpa concentrates.

The technology is also gaining greater acceptance for primary lead smelting, with one 80,000 tpa lead plant in operation [2] and two further plants under construction. In addition, the ISASMELT™ technology is at the core of the Kayser Recycling System (KRS) for secondary copper in Lünen, Germany and the Umicore Precious Metals plant at Hoboken, Belgium [3].

The application of ISASMELT™ technology for lead battery recycling is less well known. This paper discusses the development of the technology, the plant operations at Britannia Refined Metals in the UK and Metal Reclamation Industries in Malaysia and the possible application of the technology to a large (>300,000 tpa metal) secondary lead plant.

DEVELOPMENT OF THE LEAD RECYCLING PROCESS

The main sources of feed to secondary lead smelters are automotive and industrial lead-acid batteries, with electric bicycle batteries forming a rapidly increasing component of the feedstock in Asia. Typically the batteries are crushed and separated into their components prior to further treatment. Table 1 shows the main components of a lead-acid battery of which only the separators cannot be recycled.

Table 1- Lead Acid Battery Components

Component	Grids	Battery Paste	Separators	Battery Case	Acid
Composition	Pb, Sb, Ca, Sn	PbO_2, $PbSO_4$	polyethylene glass fibre,	polypropylene	H_2SO_4 water
Weight %	25 - 29 %	35 - 55%	3.5 - 8%	5 - 8%	11 - 28 %

The ISASMELT™ secondary lead process development focussed on designing the most efficient process to treat battery paste and grid metal. To this end pilot tests were carried out at Mount Isa, Australia using a 250 kg scale ISASMELT™ pilot plant. The process that was developed and ultimately patented was essentially a single furnace, low temperature, direct smelting operation, in which a relatively pure (<0.05%Sb) soft lead was produced directly from battery paste using a high lead slag as the reactive medium. Impurities in the paste such as antimony and silica gradually built up in the slag. At a certain impurity level in slag, the slag was tapped out for subsequent treatment to produce a lead/antimony alloy. The high lead slag bath was then re-established in the furnace and the soft lead production continued.

Apart from the pilot plant work, a series of crucible-scale experiments were carried out at CSIRO, Melbourne to gain a better understanding of metal partitions and reduction kinetics [4].

The process was found to be easy to control, readily enclosed for containment of lead fume and capable of high throughputs in a relatively small furnace. The positive results from the pilot work gave MIM (now Xstrata) sufficient confidence to apply ISASMELT™ technology at its subsidiary plant Britannia Refined Metals at Northfleet, UK.

THE BRM LEAD RECYCLING PLANT

Introduction

The main business of Britannia Refined Metals (BRM) is to refine the primary lead produced at Mount Isa, Australia. However a secondary lead refinery was located on the same site up to 2004. Prior to 1991, the refinery produced 10,000 tpa of lead using a short rotary furnace. In 1991 BRM upgraded the plant to produce 30,000 tpa of refined lead and lead in alloys. This upgrade enabled BRM to meet its requirements to reduce operating costs, minimise emissions of lead and minimise the quantity of final slag requiring disposal.

The chosen technology was as follows:-

- Mechanical battery breaking, separation and paste desulphurisation using the Engitec CX process
- ISASMELT™ furnace to smelt battery paste and grids to produce soft lead plus a lead antimony slag
- Use of existing rotary furnace for slag reduction to produce a lead/antimony alloy plus final slag

A flow sheet of the BRM Secondary Operations is shown in Figure 1.

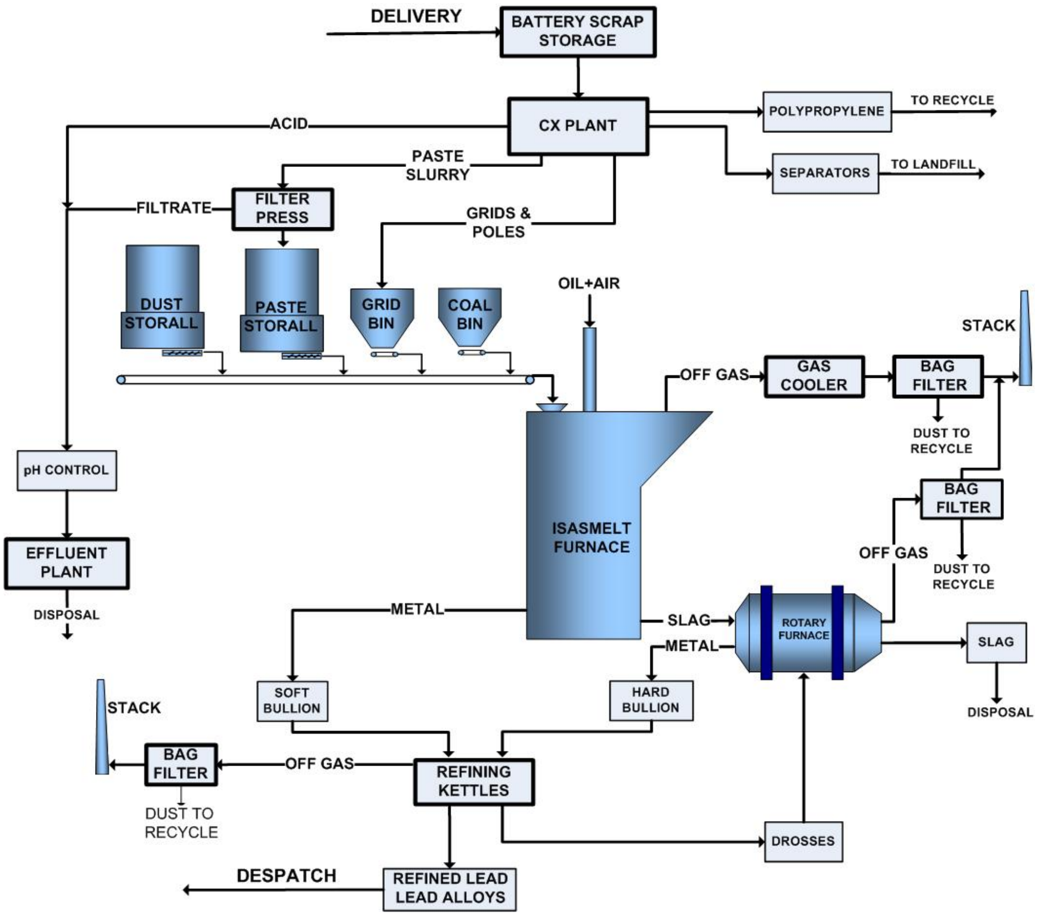


Figure 1– Britannia Refined Metals Secondary Operations Flow sheet

Battery Breaking and Separation

The Engitec CX system was designed to crush and process whole, undrained automotive batteries. Prior to initial crushing in a hammer mill, free acid recovered from scrap storage was collected, filtered and neutralised before transfer to the effluent plant. The crushed battery materials were wet screened to separate the paste from the metallic and other components. The paste fraction passed through a 0.6mm screen to a densifying collection tank and then via batch transfer to the desulphurisation tanks. The metallic lead, case material and separators were fed to two stages of a hydrodynamic (sink/float) separator from which each fraction could be collected separately. The polypropylene was sold, while the grid metal was either smelted in the ISASMELT™ or melted in the rotary furnace.

Paste Desulphurisation

The paste slurry was pumped from the densifying holding tank into either of two desulphurisation tanks. Sodium hydroxide solution (50%) was mixed with the paste which reacted to form lead oxide and sodium sulphate solution. The lead oxide was then recovered by filtration through a filter press and delivered to a rotating Storall bin from which the paste was extracted by screw conveyor and charged at a controlled rate to the ISASMELT™ furnace via a weigh belt.

ISASMELT™ Furnace Operation

The BRM ISASMELT™ furnace consisted of a vertical, refractory-lined cylinder, approximately 1.8m in internal diameter with ports in the roof for feed entry, lance entry and off gas venting. The soft lead products and high-antimony lead slag were tapped from the furnace using a single taphole and a combination of a swivel and tilting launder to direct the products to one of three pots located on rails below the tapping floor.

The battery paste and grid materials were generally treated in separate campaigns to simplify the subsequent refining process. In a typical paste campaign, a starter bath of molten paste was first formed. Paste was then fed to the furnace together with the addition of coke or coal as reductant. Reductant addition was calculated to smelt all of the paste to metal, without affecting the volume of the starter bath. The bulk of the antimony, silica, iron and other minor constituents reported to the slag phase. The lead in paste was reduced to form a low antimony (0.01- 0.1%) bath of soft lead which was tapped from the furnace at intervals into pots, from where it was transferred in the molten state to the refinery kettles. The furnace operating temperature was approximately 810ºC.

The production of soft lead continued until approximately 150 tonnes of paste had been fed to the furnace by which time the slag had become very antimony rich and contained 55-65% lead oxide. Although this slag could be reduced in situ in the ISASMELT™ furnace to produce a lead/antimony alloy, the ISASMELT™ throughput was maximised by using the rotary furnace to reduce the lead slag and this dual-vessel process became the normal operation. The rotary furnace also treated drosses from the refining kettles. Figure 2 shows the lead distribution in the process.

ISASMELT™ furnaces generally operate with oxygen enrichment of the lance air. At BRM the plant was designed to treat 7.7 tph of paste without oxygen enrichment but routinely treated 12 tph of paste. Grids were smelted in a separate campaign at rates of up to 35 tph to produce a soft lead (but containing higher antimony content than in the paste cycle). These throughput rates could have been approximately doubled with enrichment of the lance air to 30% O_2.

In the early years of its operation, production was limited by delays associated with feed conveying difficulties and with maintenance requirements in the CX battery breaker plant. Following improvements to the conveying system and continuous progress with the CX plant the ISASMELT™ plant exceeded its design specifications in 1995 and operations continued to improve up to 2004 when Xstrata Zinc decided to exit the secondary lead business.

There were many positive aspects of the operation including the significant improvements which were achieved in the performance of the refractory lining of the furnace despite the aggressive nature of the litharge slag. Full brick replacements were only required after the production of 60-70,000 tonnes of lead though partial repairs were required after approximately 20-22,000 tonnes of lead. The ease of operation and robustness of the process was demonstrated when, following the period of commissioning and improvements to some of the plant equipment, the secondary operations staffing was significantly reduced while maintaining the lead throughput. The smooth plant operation was assisted significantly by the two Storall feed bins (supplied by Mitchell Engineering) which were used to supply controlled amounts of paste and pugged dust respectively to the ISASMELT™ furnace. Fuel costs were reduced by using reclaimed 200 second oil instead of distillate for the lance and using natural gas for the holding burner.

One negative aspect of the secondary operation was the inability to produce a low sodium paste after desulphurisation despite the use of NaOH as reagent. The residual sodium in paste (up to 1.5%) resulted in the formation of a two phase slag in the ISASMELT™ furnace which consisted of a litharge slag containing between 55-85% lead oxide and a lower density slag of sodium sulphate containing up to 35% Na. Despite the inherent difficulties of this situation, the operators learned to deal with it by the introduction of a separate, upper taphole for the soda slag. The sodium sulphate was periodically tapped from the furnace to enable consistent control of the lead slag bath and the soft lead smelting process.

The sodium in paste could have been significantly reduced by investment in increased paste washing and filtration but in turn this would probably have necessitated increased investment in the effluent plant.

A more detailed description of the BRM plant can be found in the paper by Ramus and Hawkins [5].

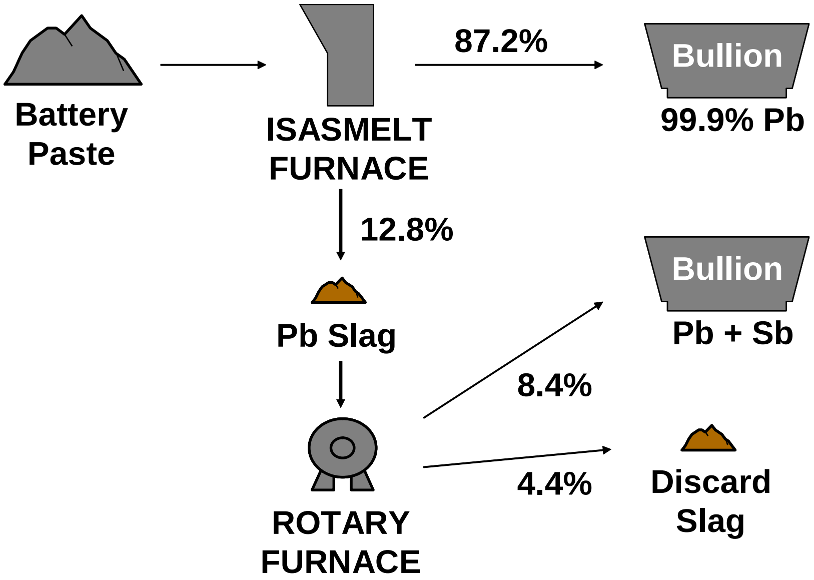


Figure 2–Lead Distribution in the BRM Process

THE MRI LEAD RECYCLING PLANT

Introduction

Metal Reclamation (Industries) Sdn. Bhd. (MRI) has been operating a secondary lead plant in Malaysia since 1972. The technology in 1995 was based upon the use of a short-bodied rotary furnace which produced approximately 1000 tonnes per month of refined lead and lead in alloys. It was clear that this production would not meet market demands for very long and thus a long-term plan was put into place to increase capacity and meet market demands. To this end MRI purchased land outside Kuala Lumpur to relocate and expand its business. MRI chose ISASMELT™ as the most appropriate technology that would allow them to meet any future environmental requirements, with regards to sulphur emissions and slag disposal.

Plant Description

The MRI plant is designed to produce approximately 40,000 tpa of refined lead and lead in alloys from a feed consisting of over 70,000 tpa of battery scrap. Batteries are crushed and separated in a 40 tph battery breaker of local manufacture. Plastics from the shredded batteries are packaged and sold for recycling. Battery paste is mixed with recycle dust and delivered to a Storall bin to allow controlled feed to the ISASMELT™ furnace. Grids are fed from a bin using a variable speed belt feeder. Additional feed bins are used to feed coal, drosses and fluxes at controlled rates to the ISASMELT™ furnace.

The ISASMELT™ furnace is similar to the BRM furnace but has an internal diameter of approximately 2.5m. Soft lead produced in the furnace is tapped intermittently to one of two 50 tonne kettles located next to the furnace. A heel of cold lead is maintained in the kettle to quench the incoming lead. The cooled lead is then pumped to the refinery kettles. Slag from the furnace is tapped through a dedicated slag taphole and granulated and dewatered using a Paul Wurth agitated tank granulation system.

The off gases from the ISASMELT™ are cooled in two stages of evaporative cooling, cleaned using a bag filter and then scrubbed free of SO_2 in a Chiyoda flue gas desulphuriser (FGD). In the FGD the flue gas is blown into water forming a fine bubble bed where SO_2 is absorbed, oxidized by injected air, and then neutralized by ground limestone slurry. The resulting gypsum product is dewatered on a belt filter and sold.

Description of ISASMELT™ Operation

The ISASMELT™ furnace was designed to treat approximately 31,000 tpa of battery paste and 19,000 tpa of grids with compositions shown as in Table 2.

Table 2-MRI Feed Composition

Component	Paste	Grids
Pb	74.1	92.0
Sb	0.30	1.8
Cu	0.018	0.047
Zn	0.008	< 0.001
As	0.057	0.12
Bi	0.016	0.023
Ca	<0.05	< 0.001
SiO_2	1.0	1.5
Sn	0.0	0.12
S	6.5	0.69
Al	< 0.05	< 0.001

The initial process design consisted of the following steps:-

- Melting up battery paste to form a starting bath
- Smelting a mixture of paste, grids and recycle dust plus coal to produce soft lead
- Tapping the soft lead at intervals of a few hours
- After approximately 10-12 hours, ending the cycle by tapping and granulating most of the high lead slag containing the antimony and other impurities. This slag is stockpiled for future treatment
- Re-establishing the starting bath and recommencing smelting

The initial process design allowed adequate time for reducing the stockpiled slag in campaigns. The reduction steps consisted of feeding the slag into the furnace under continuous reducing conditions to achieve approximately 15-20% lead in slag while adding iron (mill scale) and lime fluxes. When the slag bath was at an adequate depth, then batch reduction was commenced to reduce the slag to <1 % lead in final slag.

The lead distribution resulting from this approach is shown in Figure 3. The final slag make is significantly reduced compared with the rotary furnace operation and has been demonstrated to pass the TCLP test. At present, however, MRI does not have an outlet for this slag and so it goes to controlled disposal.

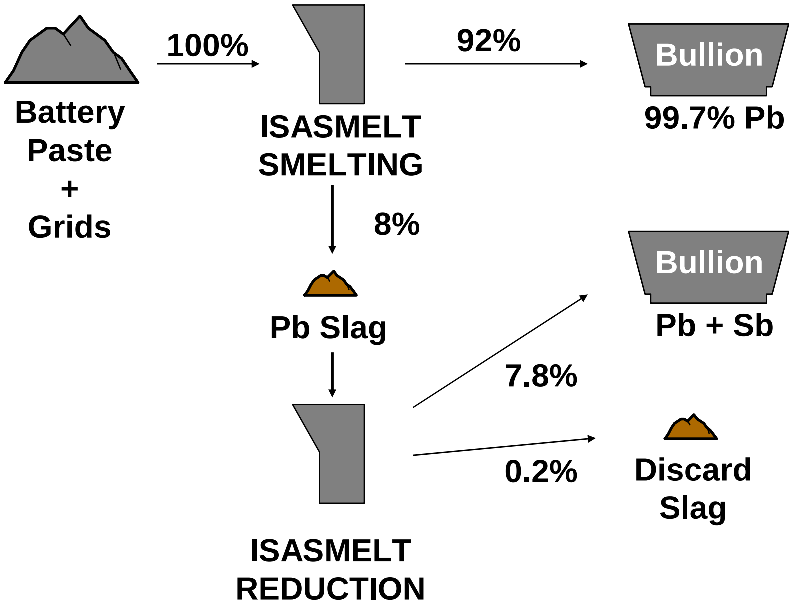


Figure 3–Lead Distribution in the MRI Process

Since commissioning in 2000, MRI has made many changes and improvements to the operation. They now find it more economical to carry out the batch reductions at the end of each smelting cycle, thus avoiding the necessity to stockpile and remelt high lead slag.

MRI has demonstrated the flexibility of their ISASMELT™ plant by using it also for the smelting of primary lead concentrates (up to the limit of their scrubbing capacity) when market conditions make it an economic proposition. When smelting primary lead concentrates, MRI have demonstrated that concentrates can be used for partial reduction of the high lead slag, followed by coal addition to complete reduction.

Additional modifications made by MRI include the use of up to 20 tpd of oxygen to increase plant capacity. A recent modification has been to convert the plant so that it can use natural gas as fuel rather than fuel oil resulting in significant cost savings.

Overall, when compared to Britannia Refined Metals, MRI has shown the advantages of flue gas scrubbing compared with paste desulphurisation. However this advantage does depend on having a market for the gypsum produced in the process. Currently, much of the gypsum produced at MRI is sold to the cement industry.

A photograph of the MRI plant is shown in Figure 4. A flow sheet of the MRI plant is shown in Figure 5.

Figure 4–The MRI Secondary Lead Plant

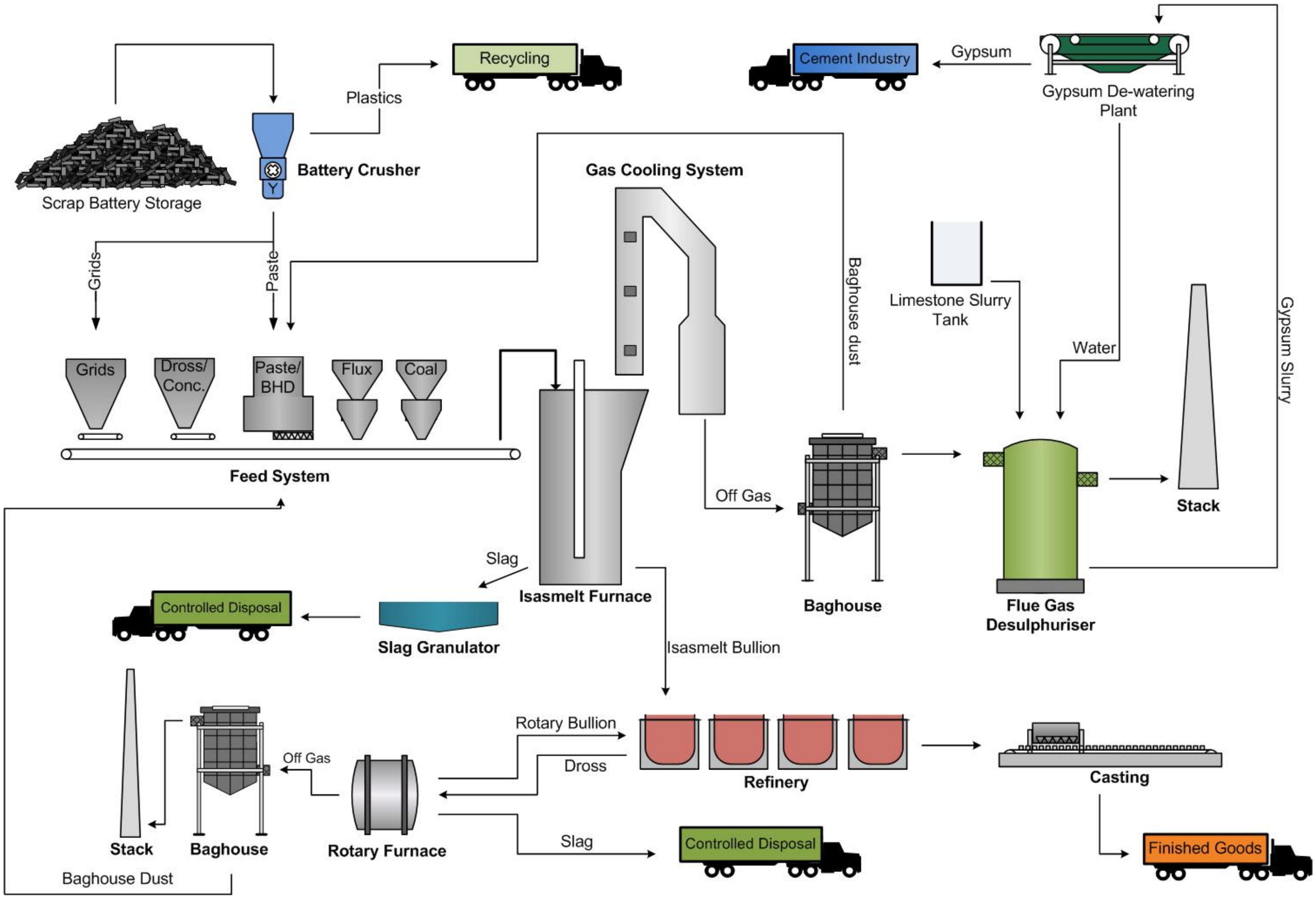


Figure 5 – Flow sheet of the Metal Reclamation Industries Operations

A 300,000 TONNES PER YEAR LEAD RECYCLING PLANT

Table 3 shows a comparison of some of the plant operating and design parameters for current ISASMELT™ plants. Of note is the wide variation in operating parameters and the relatively small furnace sizes required to accommodate the various process flows.

Table 3-Comparison of ISASMELT™ Plant Parameters

Parameter	Secondary Lead	Primary Lead	Primary Copper
Feed (tpa)	40,000 - 60,000	150,000 - 250,000	650,000 - 1,400,000
Process Air (% O2)	21 - 25%	25 - 40%	60 - 90%
Lance Flows (Nm^3/hr)	5,000 - 9,000	15,000 - 25,000	20,000 - 70,000
Furnace ID (m)	1.8 - 2.5	2.5 - 3.5	3.5 - 4.5
Sulphur Capture	Paste desulphurisation or Lime Scrubber	Acid Plant	Acid Plant

It can be seen that the throughputs in secondary lead plants are relatively small in comparison to the primary smelting plants. This reflects the nature of the secondary lead industry. Despite the fact that secondary lead comprises more than 50% of lead production annually, the business is only rationalised into relatively large smelters in North America and Europe, the largest secondary smelter probably being the Doe Run Buick smelter in Missouri with an output of approximately 145,000 tpa. In other countries there tend to be many small producers. For example there are over 240 registered lead recycling plants in India and approximately 100 registered plants in China. In addition, in most developing countries, there is a largely unregulated informal lead recycling industry competing against the regulated industry. An additional important factor is the Basel Convention banning the trans-frontier shipment of hazardous wastes including battery scrap. China, for example, thus does not officially import any battery scrap from other countries.

However, when we look to the future, we can expect increasingly strict environmental regulations and resultant closure of small operations accompanied by an increased secondary lead processing requirement. For example, the secondary lead production in China is expected to double to over 2,000,000 tonnes per year of lead by the year 2015 [6]. Under this scenario, and with increased focus on reducing hazardous emissions, large processing plants using modern technology such as ISASMELT™ are likely to become more prevalent.

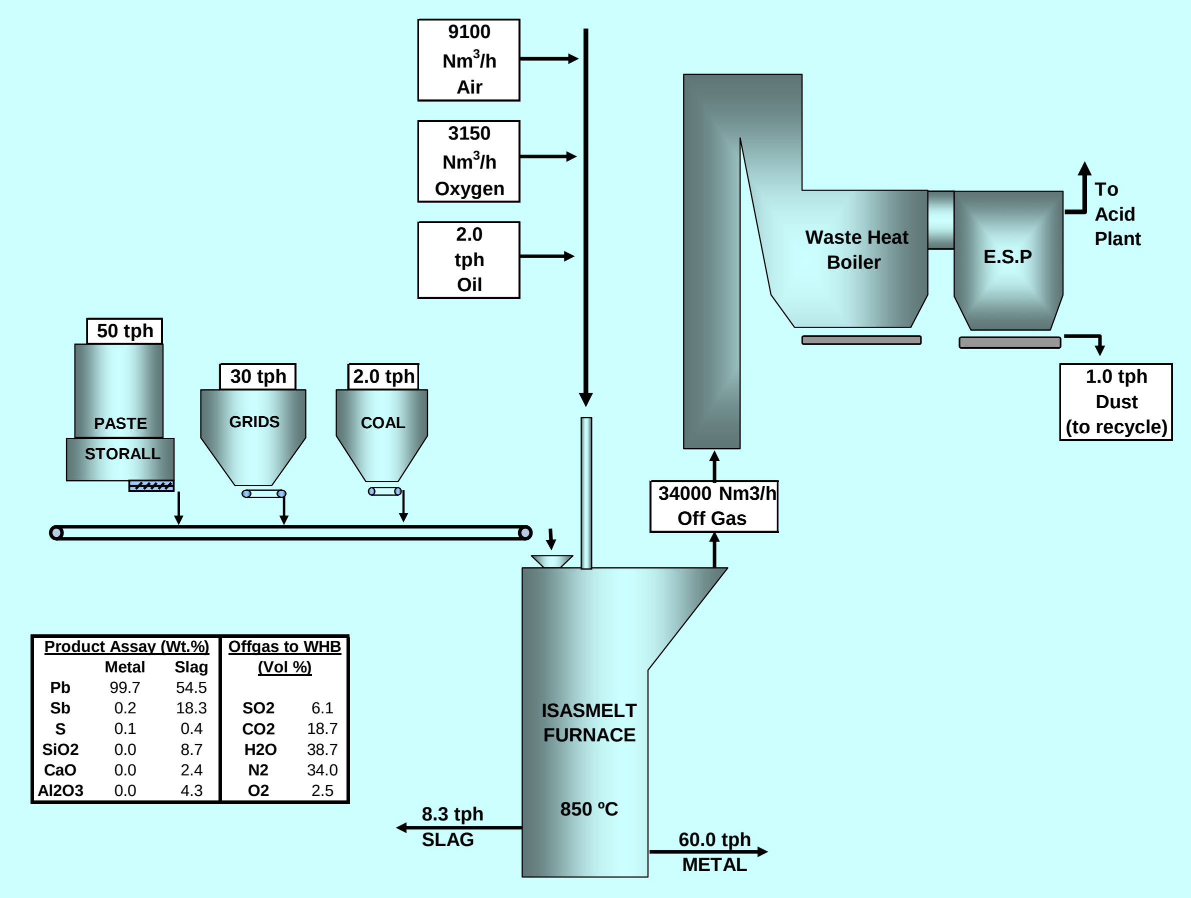
Figure 6 shows an example of the process flows for an ISASMELT™ furnace capable of producing over 300,000 tonnes per year of soft lead from a feed similar in composition to that shown in Table 2.

The main features of this operation are:

- Enrichment of the lance process air to 40% oxygen content
- Continuous production of soft lead containing 0.2% Sb or less
- Low temperature operation (<850ºC) as a result of the low-melting $PbO-Sb_2O_3$ slag
- Relatively small furnace (3.0 – 3.5m ID)
- Production of a relatively high SO_2 content in the final off gas suitable for sulphuric acid production

The high lead slag produced in the process can either be stockpiled and treated in campaigns in the ISASMELT™ furnace or can be transferred molten to a second small (<2m ID) ISASMELT™ furnace for the recovery of lead and production of a low lead discard slag plus a lead antimony alloy.

It should be noted that despite the relatively large soft lead production, this plant is still small compared to the primary smelting plants with lance flows less than one-fifth of the maximum used in primary copper smelting and a furnace volume requirement of approximately one-half of the larger copper plants.



Product Assay (Wt.%)			Offgas to WHB (Vol %)	
	Metal	Slag		
Pb	99.7	54.5		
Sb	0.2	18.3	SO2	6.1
S	0.1	0.4	CO2	18.7
SiO2	0.0	8.7	H2O	38.7
CaO	0.0	2.4	N2	34.0
Al2O3	0.0	4.3	O2	2.5

Figure 6 - Process Flows for a 300,000 tonnes per year Secondary Lead ISASMELT™ Plant

In conclusion, the application of ISASMELT™ technology for the production of secondary lead has been very positive, with the technology demonstrating the following advantages compared to the traditional rotary furnace operation:

- direct production of both soft lead and antimonial lead alloy giving blending flexibility
- ability to produce non-leachable, silicate-based, low lead discard slags
- good process hygiene due to an enclosed vessel run under negative pressure
- single furnace operation capable of any likely future plant capacity requirement

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